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THE LIFE HISTORY OF A DOCTRINE.[1]

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THIS is the season of congratulation, and even if it were not, I should begin by congratulating my fellow members upon the present condition of our Society. We have every reason to be gratified. Statistics do not always convey a clear idea of the actual state of an organization, but they may be suggestive. The last annual meeting of the Society that was held in Washington occurred in 1897, just five years ago. At that time we had 1156 members. To-day the number has grown to 2176. The membership has nearly doubled. In 1897 the number of pages in the Journal of the Society for the first eleven months was 1315, while, for the corresponding period of this year, 2489 pages were published. To be sure, this included for 1902 the general index and the twenty-fifth anniversary volume. Omitting these, the figures are, for 1897, 1246, for 1902, 1956—an increase of 710 pages in five years. Any more rapid increase would almost be alarming.

One point suggests itself in this connection. Some of you may ask whether, under existing circumstances, it is desirable that there should be two journals in this country devoted to chemistry. Perhaps I am not the proper one to discuss this subject. There

[1] Presidential address delivered at the Washington meeting of the American Chemical Society, December 30, 1902.

seems to be an increasing demand for the American Chemical Journal as well as for the Journal of the Society. Having been in existence for nearly twenty-five years and being in robust health, the thought of giving up the ghost does not appear attractive to the former. It should, however, be clearly understood that there is no rivalry between the two journals, except such as may legitimately exist between friends, causing both perhaps to try to do their best. In these days of consolidation, the question may fairly be asked whether it would not perhaps be better to unite the two? It may be said that this subject has often been under friendly consideration, but the result has been unfavorable to consolidation. It must be confessed that the personal element enters into the discussion to some extent, and your speaker is the person involved. I feel more or less as though the American Chemical Journal were one of my children. Much of my activity has gone into the Journal for a quarter of a century. I have seen it develop from a feeble condition, through a dangerous second summer, through the usual list of children's diseases, until it was able to stand on its own feet and become self-supporting. While marriage is perhaps now in order, it is clear that this would involve a change of name and a loss of identity, and this I do not like to contemplate. So, my brethren of the Chemical Society, I ask you to bear with me for a few years longer. This independent journal will do our Society no harm. On the contrary, you may count on me to do all in my power to further the interests of the Society. One new reason why I do not want to give the journal up is that by force of circumstances I have, to some extent, recently been drawn away from my chemical bearings, and I do not wish as yet to occupy that position on the shelf that is, I suppose, awaiting me. My interest in chemistry is, I think, as great as it ever was, and I wish to do everything I can to keep up that interest. Through the journal I am necessarily kept more or less in touch with many of the active workers. While this is of no special importance to the workers, it is most helpful and refreshing to me, and, after a service of over thirty years in the ranks, I feel that I have a right to a pension. The only one I ask is the permission to continue as editor of my old journal without being subjected to the suspicion that I am an enemy of our Society and its constantly improving and now excellent Journal.

But this is all too personal, and I now pass to something impersonal. The general subject to which I ask your attention may be called "The Life History of a Doctrine". This title suggests a biological analogy. The life history of an animal includes a record of the events in the life of that animal from the earliest stages to the end—from birth to death. But there are events before birth. The life history is preceded by the embryonic history, and there are events after death—events biological, as shown in heredity; events chemical and physical as shown in decay and the reduction of the complex constituents of the animal to simple forms that can be assimilated by living things and thus enter again into the round of life. I do not refer here to spiritual events after death, for, in speaking of animals, I have not had man in mind, and it is customary, I believe, to deny to all animals, with this exception, the persistence of the spirit after death. In the analogy that I have in mind, however, the spiritual events are to be taken into account, for, as I think can be made clear, there is a life after death in the case of a good doctrine as in the case of a good man. The pursuit of this analogy is interesting (to me), but it will be more profitable to illustrate it by examples, of which there is no end. I wish especially to point out the bearing of the philosophy of the history of chemistry upon the present-day problems so far as this may be possible in the time at my disposal.

The doctrine of the transmutation of metals played a most important part in its day. No one can trace it to its beginning. It is, however, clear, that it developed great strength and controlled the intellectual activities of the leading intellectual men of the world for several centuries. It led to the development of chemistry. The alchemists were the working chemists of their day. They taught the world the lesson that it is only by contact with the things of this world that we can gain knowledge of them. They laid the foundations of experimental science. The soul of alchemy was experiment. The fundamental doctrine of alchemy, transmutation, after a long and active life began to show signs of weakness; and in due time it took to its bed, and in spite of admirable medical care it died and was buried. No chemical doctrine has had anything like as long a life as this. To be sure, this could not have been possible, as the life history of the doctrine of transmutation covered a period longer than that which has elapsed since its death, though it is difficult to fix the time of its death

with accuracy. It is dead now at all events, and we may ask the question: What came after death? The doctrine accumulated large wealth and left the world a large estate. I need not give you the inventory. Probably no one can do so. But we do know that we owe to the activities of those who were controlled by the doctrine of transmutation a long list of substances that are of fundamental importance, such as sulphuric acid, nitric acid, phosphorus, alcohol, ether, etc. This is the material side of our inheritance. How about the spiritual? I have said that experiment was the soul of alchemy. That will live forever. I should perhaps have said that experiment was one of the souls of alchemy, for I suppose it is not objectionable to assume that a doctrine may have more than one soul. The rule in regard to human beings seems to be perfectly simple, and it is generally accepted, but I once heard of a professor, who, speaking of some great disaster, said: "On this occasion three hundred souls perished—counting one soul to each body." Assuming that a doctrine may have more than one soul, I am inclined to think that a second soul of alchemy is to be found in the idea of the relationship between the elements—an idea that persists and keeps dangling before us the possibility of the transmutation, not only of base metals into gold or silver, but of all the elements one into the other from one end of the list to the other.

Let us take another doctrine—that of phlogiston. The embryology of this doctrine has not been clearly worked out, but its life history has been traced pretty carefully. We know how it died and, in the events that followed, it is not difficult to find evidence of its existence after death. It was through the influence of this doctrine that chemists came to recognize the common features of those phenomena that we now group together under the general name of oxidation. They were all ascribed to one cause, a subtle substance, phlogiston. The search for this substance became the great problem of chemistry. The possibility of finding it was a great incentive to work. What matters it that the doctrine of phlogiston became aged and died and was buried? It did good service—inestimable service. It kept its disciples at work and led them through this work nearer and nearer to the truth. In its life it passed through the period of infancy with all its attendant dangers, through the period of enthusiastic youth, through

sturdy manhood, and it reached old age with its attendant signs of weakness and decay. It died at last, but only after a mighty struggle. The act of dying was prolonged. Since then generations of astute teachers of chemistry have pointed out to their perhaps even more astute scholars the errors of phlogisticians, and they have all smiled and wondered how these deluded men could ever have been deluded. Possibly they forget that those at whom they smile were the leaders of their times, and that these leaders were trying as earnestly as the chemists of our own day to learn the truth.

What is the spiritual part of the doctrine of phlogiston that lives after its death? Clearly it is the idea that all the phenomena of combustion, including calcination, have a common cause. That cause has, to be sure, been shown to be oxygen. The phlogisticians thought that the cause was phlogiston, a purely imaginary substance. Priestley and Scheele and Lavoisier showed that it is an invisible gas working quite differently from the way the phlogisticians supposed. The life of the doctrine of phlogiston left us richer in material possessions and in ideas. The discovery of oxygen which is no doubt the most important discovery ever made in the field of chemistry, tended to give a materialistic trend to the thoughts of chemists. Both the philosopher's stone and phlogiston were imaginary substances that were sought in vain. Although both have been described by enthusiastic, but inaccurate, and perhaps mendacious, workers and writers, neither of these subtle things could be found. It was, nevertheless, possible to *believe* in their existence and to indulge in the hope of their discovery. But now oxygen came on the scene. Indeed, it may be truly said that it took possession of the stage, and it has been playing the leading part in the field of chemistry ever since. Here is an invisible substance existing in the air and capable of bringing about the most astonishing changes in things. We can not realize the effect of this discovery upon the thoughts of chemists. I sometimes feel that I should like to have lived as a chemist in the latter part of the eighteenth century. What thrills the workers of that time must have felt when they heard of the discovery of oxygen and learned from Lavoisier what part it played in combustion! We sometimes plume ourselves upon the doings of our own times. Has there ever been a more active or

more fruitful period in the history of chemistry than that wonderful period here referred to?

It was a great step forward to show that oxygen is one of the most powerful agents at work in the processes that are in progress on this earth. Not only combustion, but life in all its forms is in some way dependent upon it—animal life directly, plant life indirectly. Oxygen is the controlling factor in all the changes that are familiar to us. Some one, I do not know who, is responsible for that superficial and much quoted phrase "Without phosphorus no thought." The same statement could be made with equal truth in regard to other elements, such, for example, as nitrogen, carbon, hydrogen, sulphur, sodium, calcium, and, above all, oxygen. Indeed, we may almost say, without oxygen no chemical activity on this earth. This sudden appearance of oxygen and the recognition of its importance tended to put matter on a throne. "The study of material things will lead to the discovery of the hidden causes of other phenomena. See what the discovery of oxygen has done for us! Here is something tangible. Let us to work. There must be plenty of other things that operate as causes. If we can only bring these things to light, we shall be able to understand what is going on around us." So must the materialists have thought. There were, however, in those days, as there probably always have been, those who looked for the power behind the throne on which matter had been placed. To drop the figure and return to oxygen we may say that, while the discovery of this element gave the answers to many questions, it raised many new questions; and the attempts to answer these led again to regions of imagery.

One of the oldest tricks of the mind is the invoking of spirits in time of need. What causes all bodies to attract all others? We say gravitation, and somehow this spirit helps us. We feel as though we knew more about the phenomena of universal attraction when we have given a name to an imaginary and immaterial cause. So, too, when we inquire why oxygen causes the changes it is known to cause we can only conjure the spirits and give a new name. Oxygen unites with carbon; the carbon burns; a new thing is formed. It all becomes clear when we are told that it is chemical affinity that does it. Chemical affinity isn't an imaginary substance; it isn't something that we may see and handle. We haven't forgotten the philosopher's stone and

phlogiston. Our imaginary cause is spiritual; it is not material. But this is a digression. It was intended to show how the mind reverts promptly to the subtle, however powerful the attraction of matter may be. We cannot, if we would, keep to things material.

Recalling, what perhaps even I have forgotten, that my theme is "The Life History of a Doctrine," I propose, now that I have tried to show what is meant by this phrase, to move on more rapidly, so that I may dwell somewhat more fully upon one particular doctrine that has been before the chemical world in one form or another for about a century.

The discovery of oxygen did not lead directly to the introduction of a new chemical doctrine. Its chief result, as far as doctrine is concerned, was the death of the doctrine of phlogiston.

The discovery emphasized the importance of taking into consideration the weights of the things worked with. It was by this means that Lavoisier achieved his brilliant success. That weight was rather lightly regarded in earlier days may be seen from the following quotation, which is taken from an essay by Dr. Jean Rey, published in 1630:

"My chief care hitherto has been to impress on the minds of all the persuasion that air is heavy, inasmuch as from it I propose to derive the increase in weight of tin and lead when they are calcined. But before showing how that comes to pass, I must make this observation—that the weight of a thing may be examined in two ways, *viz.*, by the aid of reason, or with the balance. It is reason which has led me to discover weight in all the elements, and it is reason which now leads me to give a flat denial to that erroneous maxim which has been current since the birth of philosophy—that the elements mutually undergoing change, one into the other, lose or gain weight, according as in changing they become rarefied or condensed. With the arms of reason I boldly enter the lists to combat this error, and to sustain that weight is so closely united to the primary matter of the elements that they can never be deprived of it. The weight with which each portion of matter was endued at the cradle, will be carried by it to the grave. In whatever place, in whatever form, to whatever volume it may be reduced, the same weight always persists. But not presuming that my statements are on a parity with those of Pythagoras, so that it suffices to have advanced them, I support them with a demonstration which, as I conceive, all men of sense will

accept. Let there be taken a portion of earth which shall have in it the smallest possible weight, beyond which no weight can subsist: let this earth be converted into water by the means known and practiced by nature: it is evident that this water will have weight, since all water must have it, and this weight will either be greater than that of the earth, or less than it, or else equal to it. My opponents will not say that it is greater, for they profess the contrary, and I also am of their opinion: smaller it cannot be, since we took the smallest weight that can exist: there remains then only the case that the two are equal, which I undertook to prove. What is shown of this particle may be shown of two, three, or a very great number—in short, of all the element, which is composed of nothing else. The same proof may be extended to the conversion of water into air, of air into fire; and, conversely, of the last of these into the first."

The idea that a thing can be weighed by reason is, I suppose, an inheritance from the old philosophers who seem to have believed that all the problems of the universe could be solved by mental operations, or that any problem that could not be solved in that way was not worthy of their consideration. The first great generalization that was reached after the method of weighing was generally adopted by chemists was what we sometimes call the law of the indestructibility of matter, or, in more refined language, the law of the conservation of mass. Then followed the laws of definite and multiple proportions. Now a law of nature is quite a different thing from a doctrine. A law once discovered does not wither and die. It is eternal. Such a statement cannot be proved to be true. It calls for faith, but faith is called for at every turn in scientific matters as well as in spiritual. Without it progress would be impossible. As I am trying to deal with doctrines and not with laws, let me say that doctrines call for even a larger faith than laws. The very essence of a doctrine is faith in things unseen. The discovery of the laws of definite and multiple proportions led to the thought of atoms—not the evasive atoms of the Greeks, but atoms that could, in a way, be made the subject of experiment—the Daltonian atoms. This conception appeals to some minds very strongly. It is not necessary that we should know what the atoms look like, though this is highly desirable. The atom of chemistry can accomplish the purpose for which it was conceived by Dalton by simply standing for a unit of

matter that can pass unchanged, so far as mass is concerned, through a series of chemical changes. That is all we need to think of under ordinary circumstances. Some refined thinkers have found mental objections to the atom and it has been the subject of innumerable attacks. It doesn't do some things that it appears to us it ought to do and we try to depose it from time to time. Particles that cannot be more than 0.001 of the size of an atom challenge the right of the latter to supremacy, and the novelty-seekers, the born iconoclasts, cry out, "Make way for the corpuscle; the atom has had its day." But, seriously, the corpuscle does not seem to threaten the atom of to-day or of the immediate future—say any time within the next million years. The atom may be composed of corpuscles. Indeed, I think chemists would rejoice to learn that this is the fact. On this point, let me quote J. J. Thomson, the father of the new corpuscle. Speaking of Lenard's observation that the penetrating power of the corpuscles depends only on their density, he says: "This is exactly what would happen if the atoms of the chemical elements were aggregations of a large number of equal particles of equal mass, the mass of an atom being proportional to the number of these particles contained in it, and the atom being a collection of such particles through the interstices between which the corpuscle might find its way." "Since the density depends only on the number of particles in unit volume and is independent of the nature of the resulting atoms, Lenard's result is a strong confirmation of the view that the atoms of the elementary substances are made up of simpler parts all of which are alike." I am as yet unable to form a judgment in regard to the value of the evidence thus presented, but my confidence in J. J. Thomson gives me faith in the thoughts suggested by him. As I understand it, the worst that can be done for chemistry by the corpuscle is to change the atom so slowly that it would take something like a million years to enable us to detect the change by the balance. Perhaps the atomic weights of the elements, or of some of them, are undergoing change. Whether in the course of geological ages the atoms are becoming simpler or more complex is a question that appears idle at first, and yet when we bear in mind the fact that the atoms of our day have already been subjected to a great variety of influences for ages past, and that the atoms that we know are comparatively complex, we may at least suspect that the tendency so far is towards complexity. But here

we are face to face with a problem far beyond our powers—*the action of eons upon ions.*

Even if we assume the corpuscle, our conception is still materialistic, and we have to face the question, What is matter? That is a deep question—one of the deepest that can be asked. It is not difficult to show that all definitions of matter that have been given are totally inadequate; to show that matter is a product of the imagination; that we know matter only in so far as it affects our senses, and our senses are affected only by the different forms of energy. By logic we can easily, with Ostwald, reach the conclusion that "matter and energy are not to be thought of as distinct, as, for example, body and soul." We cannot help agreeing with him further when he says: "If we attempt to think of matter as separate from the various forms of energy nothing is left. Matter is, in fact, nothing but a group of different energies in space." But what is energy? This question would have been promptly referred to the physicists by the older chemists, but the chemists of to-day are physical chemists or chemical physicists, and they grapple with such questions without reserve. Perhaps the nearest approach to an answer is that of Herz, who, according to Ostwald, "expressly declines to see anything in the electromagnetic theory of light but a system of six differential equations." By means of mathematics, relations may be expressed and the story of nature told in a way that is clear to one who understands the language, and perhaps the time will come when men will have a complete record of the various forms of activity of nature, and they may then see that our mechanical and materialistic conceptions of natural phenomena are like the rude drawings of a child as compared with the paintings of Raphael. We have glimpses of such a scientific millenium in a few nooks and corners of physics. When that time shall come the physicists and chemists will in a way be superfluous. Everything will take the form of mathematics. By mental operations alone it will then be possible to solve such problems as may remain to be solved. It will then no longer be necessary to work with things—or rather with those manifestations of energy which in by-gone ages (say the twentieth century) had been crudely interpreted as indicating the existence of matter. A few models of molecules, of atoms, of corpuscles, and, I fear I must add, of ions, may then be preserved

in the archaeological institutes for the contemplation of mathematical philosophers.

What I have just said has not been intended as a criticism of any tendency. I have had that vision as others have. So, too, I have had visions of a heavenly kingdom to come, and I am thankful that this has been vouchsafed to me. But that heavenly kingdom is far away and so is that scientific millenium. Meanwhile there is work to be done here on earth and with earthly things. If we were all angels, a good many problems that now worry us would be solved—never to be solved again. So, too, in that scientific millenium such work as scientific men now do will not be called for. I sometimes think that the man with the distinctly mathematical mind must necessarily be unhappy if he applies himself to the study of natural phenomena. The points of contact between his language and the facts established are relatively so few that he must have sensations like those of a man with large wealth in a desert island. I once knew a young mathematician, even then distinguished, who had made something of a study of physics. He needed to add to his income and an opportunity offered itself to him to coach some students of physics. He tried this and had to give it up. One evening I found him in great distress. He told me that he had been trying to explain the law of falling bodies to his scholars and had failed to make any impression on them. He confessed that he himself had no conception of the significance of the law except as it appeared to him in a mathematical expression. He could not think of a falling body as such. The mathematical expression $\frac{dx}{dt} = gt +$ constant, however, made all clear. He tried to convey his own thoughts to his students and he was greeted with open-mouthed wonder. So, too, I knew a physicist who approached his problems in much the same way. He would not let his class of beginners work with a lever and deduce the law from the results of their own experiments, which to me appeared an instructive exercise, "for" he said "the lever is a mathematical instrument and it is not necessary to experiment with it in order to determine the laws of its action."

On the other hand, I have been told that Lord Kelvin says he cannot form a clear conception of any natural phenomenon without the aid of a model. I remember years ago, when he was

lecturing at the Johns Hopkins University, that he showed his hearers a beautiful model of light waves, and I am sure they had the power to convey light to a number of brains that would have been in darkness if any other method had been adopted. Whether we will or not, we have the non-mathematical mind to deal with, and this brings me back to chemistry and that special doctrine of chemistry that has to deal with atoms.

The doctrine of atoms is still alive though it came into being about a hundred years ago. It has been proved to be illogical as the ether that fills all space has been shown to be incapable of existence. Properties must be ascribed to the atom that it cannot possess and the same is true of the ether. What are we to do? Throw over the atom and the ether? Although both have been convicted of being illogical, I do not think it would be logical to give them up, for they are helpful in spite of their shortcomings, and in some way they suggest great truths. They are symbolic. It would be as illogical to give them up as it is, in my opinion, to deny the existence of a power in the universe infinitely greater than any of the manifestations familiar to us; infinitely greater than man; a power "that passeth all understanding." The atom helps us; the ether helps the physicist. We cannot give them up without losing our hold on many phenomena. For a century the phenomena of chemistry have been interpreted in terms of atoms. Take away that conception and, though it would be possible to deal with these phenomena, I cannot believe that they would appear as clear as they now do. In an address before the chemical section of the British Association for the Advancement of Science last summer Professor Edward Divers took as his theme "The Atomic Theory without Hypothesis." Let me quote a few passages from his address. He says: "The atomic theory of chemistry stands unsurpassed for the way in which it has fulfilled the purpose of every great theory, that of giving intellectual mastery of the phenomena of which it treats. But in the form in which it was enunciated, and still is universally expressed and accepted, it has the defect of resting upon a metaphysical basis, namely, upon the ancient hypothesis that bodies are not continuous in texture, but consist of discrete, ultra-minute particles whose properties, if known, would account for those of the bodies themselves. Hence it has happened that, despite the light it throws upon the relations of chemical phenomena and the simple means it affords of ex-

pressing those relations, this theory has always been regarded with misgiving, and failed to achieve that explicit recognition which its abounding merit calls for. Indeed, the desire has been expressed to see the time when something on a more solid foundation shall have taken its place." Professor Divers thinks that in dealing with chemical phenomena we can avoid thinking of discrete particles of matter. The law of constant proportions is, to be sure, entirely comprehensible as a law without the aid of the atomic theory, and so is the law of multiple proportions, but can we possibly, as yet, coordinate them without this aid? I do not think I can, and this doesn't worry me. The kind of atom that my mind's eye sees seems to help me, but that eye has not troubled itself with other attributes of the atom than that one which is needed. It will be remembered that in Dalton's time it was proposed to substitute for the atom the equivalent and some even wanted to use the conception of combining numbers. This last conception appeals to the systematic mind at first, but one cannot go very far with it without tacitly accepting the atomic theory. On this point Professor Divers says: "Refusing to commit themselves to belief in the hypothesis, chemists have thought from the first to escape the adoption of the atomic theory by putting Dalton's discovery into something like these words: Numbers, called proportional or combining numbers, can be assigned to the chemical elements—one to each—which will express all the ratios of the weights or masses in which substances interact and combine together. Perhaps," says Professor Divers, "the atomic theory is successfully set aside by expressing what is an actuality as an unaccounted-for possibility. But then those who use any such mode of expressing the facts without reference to the theory, never fail also to adopt the doctrine of equivalents, and thus, by this double act implicitly give in their adherence to the theory."

While the atomic theory can be used without using atoms, this must involve a great effort for the average mind. Why should we make the effort? If we can get a broader and deeper and clearer view of chemical phenomena by making the effort, by all means let us make it. Can we? That is the whole question. Apparently, not enough chemists have made the effort to furnish us with the necessary data upon which to base a conclusion. I should like to ask a dozen chemists to give me each his idea of the atom. The results would be interesting. Some years ago I sat

next the late Bishop Brooks at a dinner party, and I had an extremely interesting conversation with him. I remember many things he said and, as having some bearing on the question I am now dealing with, I quote this remark: "I am sure", he said, "that every individual has a different conception of God. If we could get at these conceptions we should probably be greatly surprised to find how markedly they differ from one another." Each individual injects his own personality into his conceptions, and the conceptions change according to circumstances.

At first, weight, or, more accurately, mass, was the only attribute of the atom that needed to be taken into consideration, except, of course, that power of combining with other atoms which is its fundamental attribute. Soon after the atom came to be a part of the chemist's equipment, two important attempts were made to add electrical charges to the atoms. Davy and Berzelius took different views of the way in which the electrical charges led to chemical acts, but they both agreed that chemical acts are essentially electrical. Every atom had, not only weight but an electric charge which did not add to its weight, but helped to explain its activity. The atom bore this charge for many years. It was thought that it gave it up and returned to its original simple form when the dualistic conception of the constitution of compounds gave way to the unitary conception. When it was found that chlorine, an electro-negative element, could take the place of the electro-positive hydrogen without creating any marked disturbance, chemists thought it best to turn their backs on the electro-chemical theory. In fact, the old electro-chemical theories in their original forms were untenable, but this is quite a different thing from saying that electrical charges have nothing to do with chemical action. It appears to-day that these electrical charges are the controlling factors in chemical phenomena, but of that farther on.

The next change that took place in the conception of the atom was that which followed the discovery of Frankland that there is a limit to the number of atoms that can combine with any other given atom. This was followed up by Kekulé and the doctrine of valence was the result. Atoms differ from one another in respect to the number of other atoms with which they can combine. It would be interesting to follow the life history of this doctrine of valence. It has had a most eventful career. It has been chastened

by experience, and now it appears to us freed, to a great extent, from the faults of youth. It is far from dead. Indeed it is probably at the beginning of its career. The phenomena of valence must be reckoned with and the study of these phenomena carries us back to the atoms and leads us to seek in them the causes of the differences in the composition of the compounds which are formed by their union.

It has unquestionably been shown that the original form of the doctrine of valence is not tenable. Elements cannot be classified rigidly under a few heads as univalent, bivalent, trivalent, quadrivalent, etc., nor can we hold the other view that all the elements have either an even number or an odd number of valences or bonds, though there appears to be some truth in this latter view. The artiads and perissads of our youth may return to us, but before they are received it will be necessary for us to ask them a few questions, and for them to answer them satisfactorily. In fact, we have learned that the phenomena of valence need to be studied carefully before we can discover the laws that govern them. The views that prevail to-day are but the foreshadowing of a broader conception of valence. This subject is very much to the front at present. The speculations of Werner with reference to complex inorganic compounds have awakened wide interest and have set many to thinking. One cannot ignore the mass of evidence put forward by Werner that tends to show that in many compounds it is necessary to assume the existence of a core or inner sphere consisting of a group of atoms in combination, this core holding in combination a definite number of atoms or groups. Whether that which holds together the atoms that make up the core is what in simpler compounds manifests itself as valence remains to be seen. At all events, if the views of Werner should prove to be correct, we shall have two kinds of valence to deal with—that of the inner sphere and that of the outer sphere, or that of the core and that of the shell. In a recent article Werner extends his views and introduces the conception of secondary valences. Thus he holds that in ammonia the three valences that enable the nitrogen atom to hold the three hydrogen atoms in the molecule of ammonia are different from that which enables ammonia to combine with a molecule of hydrochloric acid. The former he calls the "primary valences" (Hauptvalenzen), the latter a "secondary valence" (Nebenvalenz). He does not think

that the two differ fundamentally. So Thiele in his study of the phenomena of saturation among organic compounds is obliged to assume the existence of "partial valences (Partialvalenzen), and the facts described by him are singularly in accord with the assumption. This applies up to the present only to the compounds of carbon. Thiele's "partial valences" are, however, not to be confounded with the secondary valences of Werner or the other earlier "residual valences" of Armstrong. A discussion of this subject might be made interesting and profitable, but I cannot go into it here. So many curious valence phenomena have been observed of late that one cannot help feeling that we are about to have a revelation that will make the old as well as the new phenomena appear clear. Carbon is bivalent and quadrivalent. That has always been clear, though Nef has made it clearer than it used to be. But now comes trivalent carbon that Gomberg has shown us, and we may be prepared for almost anything. And oxygen that has been regarded as a very model of bivalency these many years is getting restless, and is beginning to show that it too can do the unexpected. It seems clear that it can act as a quadrivalent element, but, according to Walden, it has even higher powers.

Whatever may come of all this, it is clear that we must enlarge our conception of the atom. It not only has the power to combine with other atoms, but under given conditions it has a definite number of such powers. If we attempt to represent these powers to our minds we can only use the grossest methods. The union of two univalent atoms does not necessitate the conception of direction. But when two univalent atoms unite with one bivalent atom we can hardly avoid thinking of two points of contact on the bivalent atom and of two directions in which it exerts its powers of combination. This conception of direction is, further, forced upon us by a study of the phenomena of stereochemistry, especially in the field of the chemistry of the compounds of carbon. But, if the carbon atom exerts its powers of combination in definite directions that can be determined by observation, it is, to say the least, highly probable that all other elements act in the same general way, and indeed many facts have been discovered within the last few years that have given a clue to the stereochemistry of nitrogen, of sulphur, of silicon and other elements. Indeed, in the studies of Werner, already referred to, stereo-

chemical phenomena are illustrated in many ways by compounds of platinum, palladium and other metals that enter into the complex inorganic bases.

Our imaginary atom then has mass. It has the power to combine with other atoms under the proper conditions. This power is either a unit as in the univalent elements, or it is divisible by 2, 3, 4, 5, 6, 7 or 8 in the case of other elements. Further, one and the same element may exhibit different powers under different conditions, but the laws governing these variations are not known. Finally, the powers of combination of a polyvalent atom are exerted in definite directions that can to some extent be determined. These directions are evidently subject to variation, and some effect upon a compound caused by displacement has apparently been shown in the case of some carbon compounds; at least Von Baeyer's strain theory is based upon this assumption.

The latest turn that has been given to the conception of the atom brings in again the electric charge. It appears that the cotemporaries of Berzelius were too easily frightened, and Berzelius was nearer right than they supposed. Every book on the history of chemistry has an obituary on the electrochemical theory of Berzelius. But now it appears that the electrical charges assumed by him must be assumed by us. These have come more and more to the front of late, and chemical union is being regarded more and more as due to the interaction of these charges. According to the modern conception, an atom may or may not be carrying a charge of electricity. When carrying its charge it is called an ion, and it is then ready for action. When the elementary ion gives up its charge, either by entering into combination with another ion, or other ions, or by being set free, it becomes an atom. But more than this. The electrical charge of an ion is either a unit charge or a multiple of this. The bivalent ion has two charges, the trivalent ion has three, etc. The experimental basis for these ideas is found in the electrolytic phenomena that are included in the scope of Faraday's law. Faraday found that a definite quantity of electricity causes a definite amount of decomposition in a conductor of the second class; and, further, he found that when the same current is passed through solutions of the salts of different metals in series, the masses of the different metals that separate are proportional to the combining weights or the equivalents of these metals. To make clear the full signifi-

cance of these facts would require more time than is at my disposal. Suffice it to say, that in terms of our present theory it takes twice as much electricity to set a bivalent atom free as to set a univalent atom free; three times as much for a trivalent atom, etc. How to conceive of one, two, three, or four charges of electricity on an ion I leave to the physicists to explain, though it must be said that they are not in the least called upon to explain.

The atom has thus been followed in its career down to to-day. The changes in our conceptions have been traced sufficiently for our purpose. It is at present a bundle of attributes and with these attributes it is a convenient nucleus for thought. Nothing has been said of the dynamics of the atom, by which I do not, of course, mean chemical dynamics in general. So far as the atom is concerned our knowledge of its motions may perhaps fairly be summed up by saying that it seems probable that it moves in some mysterious way, and perhaps the phenomena of chemistry are all due to this motion. But that carries us into the region of speculation pure and simple, and in this region the scientific worker feels uncomfortable. The atmosphere is too rarefied for him.

If you now ask what is the soul of the doctrine of atoms? I can only answer that this soul is still in the course of development. The doctrine has some immortal attributes, but what will live after its death is too early for any one to say.

"Prove all things. Hold fast that which is good."

[Contribution from the Havemeyer Laboratories of Columbia University, No. 74.]

ON THE COMPOSITION OF COWS' MILK.

By H. C. Sherman.

Received October 10, 1902.

In general the percentage of fat in cows' milk varies much more than that of the other constituents. It is probably safe to say that a variation of 3 per cent. in fat is as common as a variation of 1 per cent. in the total amount of other solids. Milk is apt to be regarded, therefore, as consisting of a serum of quite uniform composition in which is suspended a variable amount of fat. It is, however, a matter of some importance both from the physiological standpoint and as an aid in judging suspected

samples, to define as accurately as possible the normal variations of each of the chief constituents and to determine whether any change in the amount or relative proportion of proteïds, sugar or ash is connected with the fluctuations in the fat content.

With the aid of friends connected with a large dairy farm, the writer has been able to obtain a considerable number of samples, the analyses of which seem of sufficient interest to warrant publication. These samples fall mainly into two groups: (1) periodical samples of the mixed milk of a large herd, intended to show the normal variations of composition during the year, and (2) samples above or below the average in fat or in solids-not-fat, analyzed to ascertain whether any other constituent varies with the fat, and to which constituent the variations in the solids-not-fat is chiefly due.

Methods of Analysis.—The analytical methods used were those of the Association of Official Agricultural Chemists[1] and the details of manipulation were uniform throughout. Fat was determined by the paper coil method, the milk being very thoroughly dried on the coil and then extracted with anhydrous ether. The percentages of proteïn[2] were obtained by multiplying the percentages of nitrogen found by the Kjeldahl method by 6.25, the digestion with sulphuric acid being continued for about two hours after the liquid had become colorless. Ash was determined by direct ignition at the lowest possible dull red heat. Milk-sugar was determined by difference, the sum of the percentages of fat, proteïn and ash being subtracted from the percentage of total solids found by drying to constant weight in a flat-bottomed dish at the temperature of boiling water. The samples were preserved by the addition of formaldehyde in the proportion of 1 drop of the commercial 40 per cent. solution to each ounce of sample. In the experience of this laboratory the use of such an amount of formaldehyde has not been found to have any appreciable effect upon the analytical results.

Source of Samples.—All of the samples analyzed were from one large farm in Westchester County, New York. The herd contained about 600 milk cows of which about 200 were pure bred Jerseys and the rest mainly "Jersey

[1] Bulletin 46, revised edition, Bureau of Chemistry, U. S. Department of Agriculture.

[2] In accordance with the terminology adopted by the American Association of Agricultural Colleges and Experiment Stations, the term "protein" is used to designate the value (nitrogen × 6.25).

grades." From 450 to 500 cows were usually milked at a time, the others either being dry or allowed to run with their young calves. Though divided into several groups, the entire herd was under one herdsman, who stated that throughout the year each cow received hay or green fodder and one and one-half pounds of oil meal per day, and in addition to this was fed with a mixture of one-half wheat bran, one-quarter crushed oats and one-quarter corn meal. The amount of this mixture fed depended upon the judgment of the feeder and to some extent upon the season and the demand for milk, but was always liberal. Exercise was allowed freely except in very severe weather and in summer there was pasturage, though this was never depended upon to the exclusion of other food. The cattle were always comfortably housed and were milked at 4.30 to 5.00 A.M., and 3.30 to 4.00 P.M.

Morning and Afternoon Milk.—Frequent tests of the mixed milk of the herd showed that the afternoon milk contained quite regularly about 0.4 per cent. more fat and practically the same solids-not-fat as the milk yielded in the morning. Similar results have constantly been found by Richmond[1] in the great numbers of analyses made yearly in his laboratory. Moreover, it has been found at the New York State Experiment Station[2] and by Fruhling and Schultze,[3] in each case as the result of many analyses, that neither protein, sugar nor ash shows any distinct tendency to be higher at one milking than at the other, or, in other words, that the difference in composition between morning and evening milk is a difference in fat content only and does not extend to the other constituents. Linfield[4] has recently reached the same conclusion which is confirmed for the herd here studied in the following experiment by the writer.

On April 19, 1901, the milk obtained at each milking was carefully sampled and analyzed, with the following results:

	Fat.	Protein.	Sugar.	Ash.
Morning milk	4.85	3.68	4.85	0.74
Afternoon milk	5.22	3.65	4.90	0.73

Further experiments on this point were therefore considered

[1] "Dairy Chemistry," p. 128 and papers in *The Analyst*.
[2] Report for 1891; Abstracted in Experiment Station Record, **4**, 257.
[3] Quoted by Stohmann: "Milch und Molkereiprodukte," p. 166.
[4] Utah Experiment Station Bulletin 68, p. 234.

unnecessary and in studying the variations of composition from month to month only the afternoon milk was sampled.

SEASONAL VARIATIONS IN COMPOSITION.

It is well known that milk tends to be richer, both in fat and in solids-not-fat, in winter than in summer, and Richmond's analyses have shown that the milk received from English farms varies in practically the same way each year, the difference between the highest and lowest monthly averages being about the same for fat as for solids-not-fat and amounting usually to 0.3 or 0.4 per cent.

For two years, beginning with April, 1900, the mixed milk of the herd above described was sampled and analyzed once each month. As the milk came to the dairy in cans of uniform size, an accurate sample was readily obtained by means of the Scovell sampling tube. The composition of these samples is shown in Table I, below.

TABLE I.—COMPOSITION OF MONTHLY SAMPLES.

Month.	Total solids.	Fat.	Solids-not-fat.	Protein.	Sugar.	Ash.
January, 1901	14.69	5.36	9.33	3.76	4.83	0.74
" 1902	14.82	5.35	9.47	3.82	4.89	0.76
" average	14.76	5.36	9.40	3.79	4.86	0.75
February, 1901	14.53	5.24	9.29	3.67	4.87	0.75
" 1902	14.73	5.38	9.35	3.72	4.88	0.75
" average	14.63	5.31	9.32	3.70	4.87	0.75
March, 1901	14.39	5.19	9.20	3.57	4.90	0.73
" 1902	14.52	5.37	9.15	3.57	4.84	0.74
" average	14.46	5.28	9.18	3.57	4.87	0.74
April, 1900	14.25	5.14	9.11	3.48	4.88	0.75
" 1901	14.43	5.13	9.30	3.66	4.89	0.75
" average	14.34	5.14	9.20	3.57	4.88	0.75
May, 1900	14.37	5.22	9.15	3.58	4.84	0.73
" 1901	14.25	5.12	9.13	3.54	4.84	0.75
" average	14.31	5.17	9.14	3.56	4.84	0.74
June, 1900	14.26	5.10	9.16	3.59	4.85	0.72
" 1901	14.64	5.38	9.26	3.59	4.91	0.76
" average	14.45	5.24	9.21	3.59	4.88	0.74
July, 1900	14.13	5.00	9.13	3.54	4.84	0.75
" 1901	14.23	5.29	8.94	3.50	4.71	0.73
" average	14.18	5.15	9.03	3.52	4.77	0.74
August, 1900	14.11	5.00	9.11	3.58	4.79	0.74
" 1901	14.34	5.28	9.06	3.54	4.78	0.74
" average	14.23	5.14	9.09	3.56	4.79	0.74
September, 1900	14.73	5.39	9.34	3.75	4.84	0.75
" 1901	14.34	5.27	9.07	3.56	4.77	0.74
" average	14.54	5.33	9.21	3.66	4.81	0.74

Month.	Total solids.	Fat.	Solids-not-fat.	Protein.	Sugar.	Ash.
October, 1900.....	14.46	5.23	9.23	3.73	4.75	0.75
" 1901.....	14.98	5.48	9.50	3.87	4.89	0.74
" average	14.72	5.36	9.36	3.80	4.82	0.74
November, 1900	14.78	5.35	9.43	3.82	4.86	0.75
" 1901	14.81	5.32	9.49	3.87	4.86	0.76
" average ..	14.80	5.34	9.46	3.84	4.86	0.76
December, 1900	14.52	5.20	9.32	3.77	4.79	0.76
" 1901	14.77	5.34	9.43	3.85	4.81	0.77
" average ..	14.65	5.27	9.38	3.81	4.80	0.77
General average.	14.71	5.26	9.25	3.66	4.84	0.75

During the time covered by these analyses there was no change in the system of feeding or management and samples were not taken during or immediately after very sudden changes in the weather. The large size of the herd and its divisions into separate groups would minimize any variations which might be due to individual peculiarities or accidental causes, and as there were few changes in the herd and the number of fresh cows did not fluctuate very greatly from month to month, it seems safe to conclude that the differences shown by the monthly averages are due to influences very closely connected with the season and that they may be called seasonal variations.

The diagram on the opposite page is designed to show the variations here found, together with those previously reported by Richmond[1] and by Van Slyke.[2]

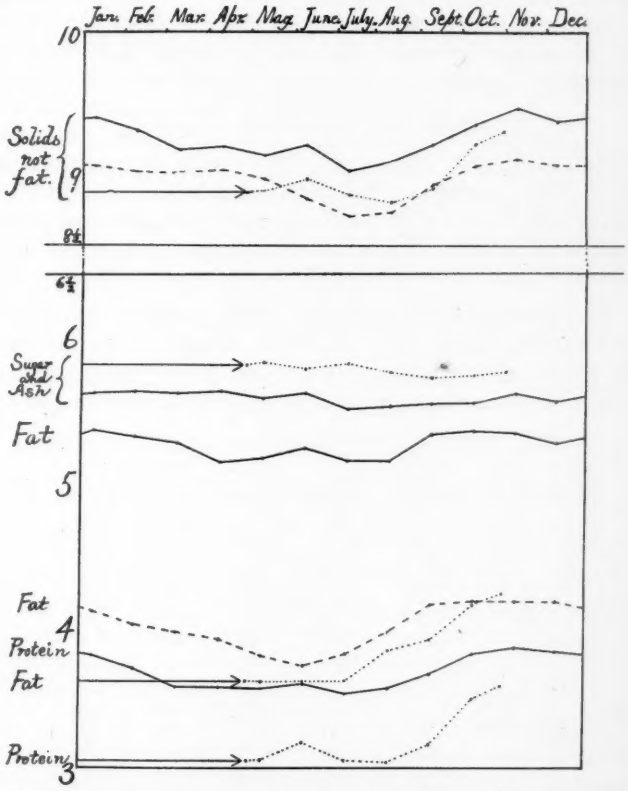
In the diagram the results above given are represented by solid, those of Richmond by broken, and those of Van Slyke by dotted lines. Richmond determined only fat and solids-not-fat. Van Slyke's analyses, while including the determination of protein, were made primarily for another purpose and cover only a part of the year.

Richmond's results for fat and for solids-not-fat run nearly parallel. As regards solids-not-fat the writer's results are practically parallel with those of Richmond. On fat, our results are similar to those of Richmond but show less decrease in midsummer. This is probably due to the fact that the herd here studied was managed with special reference to the production of milk of uniformly high fat content. The milk of this herd was

[1] "Dairy Chemistry," p. 128 (afternoon milk for 1896). Richmond's more recent analyses show monthly variations of the same character.

[2] Averages of data obtained by analysis of milk delivered to certain cheese factories during the summers of 1892–'94, summarized in the report of the New York State Experiment Station for 1894.

richer during the second summer than during the first. The results for the first twelve months would be found nearly parallel to Richmond's.



Van Slyke's results show a greater rise in both fat and solids-not-fat in the autumn, but this is explained by the fact that most of the cows in the herds observed by him had calved in the spring, so that in passing from summer to autumn we find the combined effects of season and of advancing lactation.

Considering the circumstances just mentioned, the three sets of curves show a very close agreement and in each case there is a very evident tendency for the fat and solids-not-fat to rise and fall nearly together.

Passing to the other curves we find the sugar-and-ash percentages[1] to be nearly uniform, the extreme variation between monthly averages being only about 0.1 per cent., while the proteïn runs parallel with the solids-not-fat. In other words, the seasonal variations in solids-not-fat are practically variations in proteïn, the percentage of sugar and ash remaining nearly uniform throughout the year.

COMPOSITION OF SPECIAL SAMPLES.

During the time covered by the monthly analyses recorded above several samples of milk from individual cows or from certain groups of cows in the herd were analyzed. For convenience, most of the samples from individual cows can be grouped in two classes.

Some Unusually Rich Samples.—These samples were taken at random from among many of similar richness. Table II shows the composition of these samples and, where ascertained, the daily yield of milk, and the number of months since the last calf.

TABLE II.—COMPOSITION OF SOME UNUSUALLY RICH SAMPLES.

No.	Months since last calf.	Milk per day. Pounds.	Total solids. Per cent.	Fat. Per cent.	Solids-not-fat. Per cent.	Proteïn (N × 6.25). Per cent.	Milk-sugar. Per cent.	Ash. Per cent.
1	..	..	19.88	8.96	10.92	5.11	4.95	0.86
2	10	9½	19.21	8.94	10.27	4.92	4.55	0.80
3	10	4½	18.99	8.83	10.16	4.38	4.97	0.81
4	"nearly dry"		18.74	8.14	10.60	4.81	4.94	0.85
5	7	9	18.44	7.84	10.60	4.91	4.91	0.78
6	..	12	18.24	7.72	10.52	4.87	4.87	0.78
7	2½	21	17.81	8.04	9.77	3.97	4.96	0.84
8	12	6	17.70	7.42	10.28	4.80	4.66	0.82
9	9	11½	17.70	7.07	10.63	4.96	4.84	0.83
10	10	..	17.28	7.05	10.23	4 80	4.61	0.82
11	..	10	16.83	6.98	9.85	4.59	4.45	0.81
12	3½	14	16.81	6.61	10.20	4.51	4.84	0.85
13	9	8½	16.73	7.34	9.39	4.23	4.31	0.85
	Average.....		18.03	7.76	10.27	4.68	4.76	0.83

It will be noticed that richness in fat is accompanied in each of these cases by richness in solids-not-fat, while four of the thirteen samples equal or exceed in solids-not-fat the figure given by Richmond[2] as the highest which had come under his notice. This

[1] The writer's results for sugar and ash are here combined in order to facilitate comparison with those of Van Slyke. A small variation in ash following that in proteïn will be noted later.

[2] "Dairy Chemistry," 1899, p. 120.

increase in solids-not-fat occurs almost entirely in the proteïds, which average about 1 per cent. higher in this group of samples than in the mixed milk of the entire herd. In most cases the cows were well advanced in lactation and the yield of milk was rather small. Seven of the samples were from pure-bred Jersey cows and six from Jersey-grades.

Samples Low in Solids-not-fat.—The six samples shown in Table III were all from healthy cows. The first five were obtained during the hot weather of August, 1901. The sixth was from the same cow as the fifth, but was taken three months later. This is the only case in any of the tables where two samples from the same cow are given. While these samples vary considerably in fat content, they are alike in containing low percentages of solids-not-fat.

TABLE III.—SAMPLES LOW IN SOLIDS-NOT-FAT.

No.	Months since last calf.	Milk per day. Pounds.	Total solids. Per cent.	Fat. Per cent.	Solids not-fat Per cent.	Proteïn (N × 6.25). Per cent.	Milk-sugar. Per cent.	Ash. Per cent.
1	6	10½	14.29	6.09	8.20	3.66	3.78	0.76
2	9½	11	11.97	3.71	8.26	3.55	4.00	0.71
3	2	26½	10.83	2.64	8.19	2.86	4.58	0.75
4	9	7	10.65	3.27	7.38	3.24	3.43	0.71
5	7	8	11.77	4.69	7.08	3.57	2.81	0.70
6	10	6½	9.66	2.97	6.69	3.17	2.86	0.66
	Average		11.53	3.90	7.63	3.34	3.59	0.71

The percentages of proteïds are here somewhat lower than in Table I, but are not low in proportion to the fat present. Averaging the six analyses it happens that the fat percentage is practically that which has been found as the general average for ordinary cows' milk. It is noticeable that the averages for proteïn and ash are also strikingly close to the estimated general averages, while the sugar is here considerably below the normal average. In other words, the deficiency of solids-not-fat is all in the milk-sugar. This is in accordance with Richmond's opinion[1] that "when genuine samples are low in solids-not-fat, the proteïds and ash are normal and the milk-sugar is the constituent on which the deficiency falls."

RELATIONS BETWEEN THE PRINCIPAL CONSTITUENTS.

Relation of Proteïn to Fat.—Timpe[2] announced in 1899, appar-

[1] *The Analyst*, **25**, 226.
[2] *Chem. Zig.*, **23**, 1040.

ently on the basis of less than thirty analyses, that there exists a definite quantitative relation between the percentages of fat and proteïds in cows' milk which may be expressed by the formula proteïds $= 2 + 0.35$ fat. A similar conclusion, though differently expressed, had been reached by Cooke[1] some years earlier as the result of an extensive compilation of American analyses. Cooke found that in milks containing not less than 13 per cent. of total solids, the milk-sugar is nearly constant while "the proteïds increase with the total solids, being always about one-fourth." Since the other three-fourths of the increase is practically all fat it is evident that this relation might be expressed by a formula almost identical with that of Timpe. The work of the latter was, however, strongly criticized by Richmond,[2] who gives the average results of analyses of about fifty samples grouped according to fat content and concludes that while there is a tendency for the proteïds to be higher when the fat is high, this tendency is very much less than that indicated by Timpe's formula. Comparing the average results found by Woll[3] in testing cows of different breeds, it appears that he failed to find the differences in protein quite as large in proportion to the differences in fat as the formula would indicate.

Applying to the analyses given above the formula which expresses the conclusion reached by Cooke (protein $= 2 + {}^1/_3$ fat) we find that with samples from individual cows there may be considerable discrepancies, but if we take the average milk of the herd for the year or the average of Table II or of Table III, the figure for protein given by the formula is within 0.1 per cent. of the amount actually found. To test this point further the following samples were analyzed: (1) a composite sample of the milk of 14 cows taken at random from among those low in fat, (2) the mixed milk from a group of about 100 cows which had been regularly found below the average of the herd in fat content, (3) the mixed milk from a group of about 100 cows of which a large proportion were well advanced in lactation, and (4) a sample of the mixed milk of the entire herd taken in May, 1902, when fresh pasture and a change in the grain ration had produced a temporary rise in fat content. The analyses of these samples follow:

[1] Vermont Experiment Station Report for 1890, p. 97.
[2] *The Analyst*, **25**, 225.
[3] Wisconsin Experiment Station Report for 1901, p. 85.

No.	Total solids. Per cent.	Fat. Per cent.	Protein. Per cent.	Milk-sugar. Per cent.	Ash. Per cent.
1	12.78	3.91	3.25	4.92	0.69
2	14.34	5.07	3.64	4.89	0.74
3	15.39	5.67	4.03	4.87	0.82
4	15.05	5.76	3.77	4.75	0.77

In each of the first two samples the percentage of protein is within 0.05 per cent. of that which would be calculated from the formula. In (3), where the richness of the milk was due chiefly to advanced lactation, the increase in protein is more than one-third of the increase in fat, while in (4), where the fat content was temporarily increased by a change of food, the increase in protein is less than one-third as great.

The data at present available indicate that aside from the seasonal variation already noticed, the percentages of fat and protein tend to rise and fall together, though not to the same extent, that the average relation between the two is approximately expressed by the formula, protein $= 2 + {}^1/_3$ fat, but that the protein often shows less variation from the average than this formula would imply.

Relation of Ash to Protein.—According to Richmond[1] the percentage of ash may be deduced with fair accuracy from that of protein by the formula, ash $= 0.36 + 0.11$ protein. Most of the analyses given in this paper had been made and the tendency of the ash to vary with the protein had been noticed when the above formula was published. On applying it to our results, we find a very close agreement between the percentages of ash calculated and those actually found. The discrepancies were as follows: (1) In 24 samples of the mixed milk of the herd, from $+ 0.05$ to $- 0.01$, average $+ 0.015$ per cent; (2) In 7 samples of mixed milk from groups of 6 to 100 cows, from $+ 0.05$ to $- 0.02$, average $+ 0.021$; (3) In 23 samples of milk from individual cows, four of which contained over 5 per cent. of protein, from $+ 0.12$ to $- 0.08$, average $+ 0.033$. If the formula be modified to read ash $= 0.38 + {}^1/_{10}$ protein, an even better agreement is obtained, the above discrepancies becoming, respectively, (1) from $+ 0.03$ to $- 0.02$, average $+ 0.001$; (2) from $+ 0.02$ to $- 0.04$, average 0.000; (3) from $+ 0.09$ to $- 0.08$, average $+ 0.010$.

Relation of Milk-Sugar to Other Constituents.—The analyses do not indicate that the milk-sugar has any tendency to rise and

[1] *The Analyst*, **26**, 310.

fall with any other constituent. In normal milk the percentage of sugar in the serum seems to be very nearly constant. Certainly it shows smaller relative variations than any other of the principal constituents and such variations as occur are usually so irregular as to appear accidental. Analytical errors also would be larger here than elsewhere, inasmuch as the milk-sugar is usually estimated by difference. In milk showing an unusually low percentage of solids-not-fat, the deficiency is found to be principally in the milk-sugar. Such milk may be yielded by healthy cows and is most commonly but not exclusively found in hot, dry weather. Occasionally there may be in midsummer a sufficient number of such cases to cause an appreciable lowering in the sugar content of the mixed milk of a large herd, but ordinarily there seems to be no seasonal variation in the percentage of milk-sugar such as is found in the case of fat, of proteïn, and to some extent also of ash.

SUMMARY.

As all of the samples analyzed were from one herd of cattle, the following statements, while summarizing the results which we have obtained, may not be equally applicable to milk produced under other conditions.

Monthly analyses extending over two years showed the percentage of proteïn, like that of fat, to vary with the season, being higher in fall and winter than in spring and summer, while the percentage of milk-sugar remained nearly constant throughout the year.

In general, a milk rich in fat will also be rich in proteïn. In these analyses the excess of proteïn above the normal averaged about one-third as much as the excess of fat.

All of the results obtained accord with the conclusion recently reached by Richmond that any deficiency of solids-not-fat is chiefly due to a deficiency in the milk-sugar, while any excess above 9 per cent. is chiefly due to an excess of proteïn.

In practically all of the samples examined the relation between proteïn and ash was very nearly that found by Richmond and expressed by the formula, ash $= 0.36 + 0.11$ proteïn. To agree more exactly with our averages, the formula may be modified to read ash $= 0.38 + {}^{1}/_{10}$ proteïn.

NEW YORK CITY,
September, 1902.

A CHEMICAL METHOD FOR DETERMINING THE QUALITY OF LIMESTONES.[1]

By Alfred M. Peter.

Received October 20, 1902.

The turnpike roads in the vicinity of Lexington, Kentucky, are built of the only stone which is conveniently within reach, namely: the limestone of the upper and middle beds of the Trenton formation. The character of the beds of this limestone is quite different at different levels, and it is common experience that the so-called "blue" layers are less valuable for any exposed construction than the "gray" because of their more rapid disintegration on exposure to atmospheric influences. Some beds which, when recently quarried, appear of fairly good quality are penetrated by thin layers of the blue material which disintegrate rapidly by weathering, causing the stone to separate into laminae of varying thickness. According to the writer's observation, the blue material is of two varieties; it may be quite shaly and moderately phosphatic or very phosphatic and not especially clayey, but it invariably contains easily soluble ferrous compounds and a small but very notable amount of organic matter which makes its presence known when the material is dissolved in dilute acids by the odor of petroleum imparted to the escaping gas and by the brown scum floating upon the liquid. The writer believes that the peculiar color of the so-called "blue" limestone is largely determined by the presence of a ferrous phosphate. He is of the opinion, also, that the rapid weathering down of blue material is due to the presence in it of easily oxidizing substances, such as ferrous compounds and organic matter, the oxidation of which is greatly favored by the greater porosity of this material, as compared with the gray limestone. The porosity of these blue limestones appears to increase with increasing amounts of phosphates and may in reality be dependent upon the presence of the minute spiral shell, *cyclora minuta* which, as has been shown by the writer and Professor A. M. Miller,[2] carries the phosphate. When this shell is present in very large numbers it gives to the rock a structure somewhat resembling that of chalk, though more compact. These soft limestones, and especially the shaly kind containing clay, also contain some finely granular pyrite which, by its oxidation, undoubtedly promotes disintegration.

[1] Read before the Cincinnati Section of the American Chemical Society, October 8, 1902.

[2] Eighth Annual Report Kentucky Agricultural Experiment Station, p. 25.

For the general character of the Trenton limestones of Central Kentucky reference is here made to Report A of the Kentucky Geological Survey, Vol. 2, pages 123-4. In the analyses there published of 18 samples of limestone from Trenton group in Bourbon, Clark, Fayette, Franklin, Madison, Mercer and Woodford counties, Kentucky, by Dr. Robert Peter, the silica and silicates insoluble in hydrochloric acid of 1.15 sp. gr. vary from 1.88 to 14.18 per cent., the average being 5.36 per cent., and the phosphoric acid ranges from 0.118 to 0.860, the average being 0.434 per cent. Later analyses by Dr. Robert Peter showed much higher percentages of phosphates in certain specimens.

If the writer's view of the causes of disintegration of these rocks is correct, a very good index of the relative stability of different samples could be obtained by measuring their relative amounts of easily oxidizable matters, phosphoric acid and clay or insoluble matters.

THE METHOD OF ANALYSIS.

The writer proposes, therefore, to dissolve the limestone in dilute sulphuric acid in the presence of a known amount of potassium permanganate and determine how much permanganate has been reduced during that process, after which the solution is to be used for the determination of phosphoric acid by a rapid volumetric method, and the insoluble residue, for the determination of the insoluble matter and clay.

Determination of Oxidizable Matters.—The method was actually carried out as follows: 1-gram portions of the finely powdered samples, previously dried at 100 C., were weighed into 250 cc. Erlenmeyer flasks, and 25 cc. of N/10 potassium permanganate solution measured into each and shaken until the powder was moistened; 100 cc. of a 10 per cent. sulphuric acid (110 cc. H_2SO_4 of 1.84 sp. gr. + 1800 cc. of water) was then added and the flasks again shaken. If the color of the permanganate appeared to be nearly all discharged, as happened in some of the limestones examined, a second 25 cc. of permanganate solution was added at once. Two other flasks were charged with the same amounts of permanganate and sulphuric acid to serve as checks upon the decomposition of the permanganate due to heat and acid alone. All the flasks were immediately placed upon a

boiling water-bath and allowed to remain there for half an hour, with occasional shaking, after which 30 cc. of N/10 oxalic acid was run into each, or more, if necessary, and the flasks allowed to remain on the bath a few minutes longer, until the brown manganic compounds had entirely disappeared. It is well to adjust the quantity of oxalic acid added, so that there will be at least 8 or 10 cc. in excess of what is actually oxidized, as otherwise the disappearance of the manganic compounds will be slow. Where 25 cc. of permanganate had been used, 30 cc. of oxalic acid were enough, if the reduction by the limestone had been considerable, but not if this had been only slight. The flasks were then removed from the bath and the excess of oxalic acid titrated back with permanganate solution. The amount of permanganate reduced by the easily oxidizable matters in the limestone was thus ascertained, due allowance having been made in each case for the amount reduced in the control experiments.

The presence of pyrite in these limestones has already been mentioned and it was observed in several of the samples, after the acid had been poured on. After the titrations were finished, the residues were, in every instance, examined by means of a lens, before filtering, but in no case was any pyrite apparent. It is believed that it was completely oxidized. A qualitative test with finely powdered pyrite showed that it reduced the acid permanganate solution rapidly, even in the cold, but in a quantitative experiment with 0.02 gram of pyrite, 50 cc. of permanganate and 100 cc. of 10 per cent. of sulphuric acid, only about two-thirds were oxidized, probably because the mineral was not ground sufficiently fine.

The writer proposed to make a separate determination of the pyrite in these limestones by a rapid method based upon the reaction observed by A. Rollet[1] but time did not permit.

To ascertain whether one-half hour digestion with the sulphuric acid and permanganate was long enough to obtain the whole reducing effect of the samples, a set of duplicates was made upon six of the samples, digesting them one-half and one hour respectively. The results were substantially the same, as shown below.

Cubic centimeters permanganate solution reduced by 1 gram of sample (1 cc. permanganate = 0.00078 gram available oxygen).

[1] Ref. in *Am. Chem. J.*, **2**, 69 to Dingler's *poly. J.*, **233**, 124.

	Blank.	1.	2.	3.	4.	5.	6.	Blank.
1 hour digestion	1.95	3.85	2.45	29.85	11.65	6.45	6.05	2.25
½ hour digestion	1.1	3.1	2.1	28.2	10.7	5.6	5.4	1.3
Gross difference	0.85	0.75	0.35	0.65	0.95	0.85	0.65	0.95

As the average increase of decomposition in the blank experiments is 0.9 cc., it is evident, therefore, that the oxidation was complete in half an hour. Indeed it is probable that the reaction is practically complete in the cold, or that heating for a shorter time than one-half hour would suffice, but no experiments were made to test this supposition. It is noteworthy that, when the acid is poured upon the limestone, in the presence of permanganate, the petroleum-like odor is very slight and there is no floating carbonaceous matter observable, whereas, with the acid alone, these are both very evident, as already mentioned.

Determination of Insoluble Matter and Clay.—After the titration, a drop or two more of oxalic acid was added to remove traces of permanganate, and 10 to 15 cc. of hydrochloric acid of reagent strength (20 per cent) to retard crystallization of calcium sulphate, and the solutions filtered from the residues as quickly as possible. It was difficult to obtain a perfectly clear filtrate without too much waste of time, so a slight opalescence of the liquid from suspended clay was disregarded in most cases. The residues were washed, first with a little warm, dilute hydrochloric acid, finally with water, burned and weighed as total insoluble residue. A comparison of the amounts of insoluble residue obtained in the half-hour and one-hour digestion already described, shows only a very slight decrease by the longer digestion.

PER CENT. OF INSOLUBLE MATTER.

	1.	2.	3.	4.	5.	6.
½ hour digestion	2.94	1.45	18.75	8.22	2.29	2.43
1 " "	2.88	1.48	(17.08)	8.05	2.25	2.42
Difference	0.06	—0.03	(1.67)	0.17	0.04	0.01
Average	2.91	1.46	(17.92)	8.14	2.27	2.43

Some of the residue from the one-hour digestion of No. 3 was accidentally lost before weighing, so that the difference in this case is not really as great as it appears.

In order to separate the sand and clay, the residue obtained from a duplicate determination of the easily oxidizable matter was transferred, together with the filter, without burning, to a platinum dish of about 100 cc. capacity, and gently boiled with 10

cc. of concentrated sulphuric acid for several hours, the dish being covered with a watch-glass during the operation. A small amount of potassium nitrate was added to hasten the oxidation of the filter-paper. After cooling, about 50 cc. of water were added and the contents of the dish boiled a few minutes, allowed to settle, and filtered, leaving as much of the residue as possible in the dish.

After washing this residue, it was boiled with three successive portions of a saturated solution of sodium carbonate to separate soluble silica, thoroughly washed, burned and weighed. This weight was designated sand and the difference between this and the total insoluble residue previously determined was considered clay. Qualitative tests of some of these residues showed that they were not pure quartz sand, but still contained silicates, probably feldspathic in character, as a very notable amount of potassium was present.

Determination of Phosphoric Acid.—The phosphoric acid was determined by A. L. Emery's modification of the volumetric method of the Association of Official Agricultural Chemists.[1] For this purpose, half of the solution obtained by dissolving the limestone in the sulphuric acid permanganate was used. When it is not desired to weigh the insoluble matter, this solution may be used without filtering. An independent determination of phosphoric acid was made for comparison upon the first six samples by the same volumetric method, using the solution obtained by dissolving 0.5 gram of the sample in nitric acid. The results are given below and show a reasonable agreement between the two methods.

PER CENT. OF PHOSPHORIC ACID.

	1.	2.	3.	4.	5.	6.
Solution in H_2SO_4 and $K_2Mn_2O_8$ ..	1.00	0.18	2.42	1.98	0.60	0.62
" " HNO_3	1.02	0.14	2.32	1.80	0.54	0.48
Difference.....	—0.02	0.04	0.10	0.18	0.06	0.14
Average.....	1.01	0.16	2.37	1.89	0.57	0.55

The molybdic precipitates obtained from the sulphuric acid solutions were easier to filter and wash than those from the nitric acid solution, the latter showing a great tendency to run through the filters.

DESCRIPTION OF THE SAMPLES.

In this investigation 18 samples of limestone were analyzed,

[1] This Journal, **24**, 895.

collected by the writer from stone in use upon roads near Lexington or from quarries which had been worked for such stone. The samples were chosen especially with reference to presenting the best, the worst and about the average quality of the material now actually in use for road construction in this locality. They may be described briefly as follows:

No. 1. Gray, crystalline, fossiliferous limestone; very hard; broken from an eight-inch ledge which appeared to have resisted the weather. From an old quarry on the Nicholasville road.

No. 2. Hard, gray, crystalline stone selected from a pile of broken stone on the roadside, Nicholasville road.

No. 3. Blue, slaty, soft stone, selected from the same pile as No. 2. It was already disintegrating, although it had only been exposed a few months.

No. 4. Blue limestone from the roadside; not as shaly as No. 3, but weathering in places to a soft pinkish material.

No. 5. Hard, gray, compact stone, selected from the road now in process of construction at the Lexington Fair Grounds. The superintendent of the Construction Company considers this the best stone for the purpose he has used about Lexington.

No. 6. Average of small pieces taken from the same road as No. 5.

No. 7. Hard, gray, crystalline stone, selected from a pile by the roadside on the Tates Creek pike.

No. 8. Thin, blue, slaty piece from the same pile as No. 7.

No. 9. Another slaty, blue piece from the same pile.

No. 10. Compact, hard, gray stone selected from the roadbed near the same place as No. 7.

No. 11. Average from the same place as the preceding, obtained by taking small pieces from the surface of the road where it had been exposed by washing; mostly blue limestone.

No. 12. Average of small pieces taken from a pile of crushed rock by the roadside on the Bryan's Station pike. The superintendent of the Construction Company states that the stone used on this pike is the worst he has met with about Lexington.

No. 13. Representative sample of the thin, soft, blue layers in the quarry on the Bryan's Station pike.

No. 14. Representative pieces from the thicker, soft, blue layers in the same quarry.

No. 15. Selected piece of the harder blue layers in the same quarry.

No. 16. Nearly white, very hard, concretionary masses occurring in the soft, blue layers in the same quarry.

No. 17. Thin, slaty layers from the same quarry. Disintegrate very rapidly.

No. 18. Selected piece from the hard layers in the upper part of the same quarry, which seem to have resisted weathering.

RESULTS.

The results of the analyses were as follows, calculated as per cent. of the samples dried at 100° C.

	Number.	Oxygen consumed.	P_2O_5.	Sand.	Clay.	Total insoluble.
Tough, hard, compact stone, resisting weathering, mostly gray.	1	0.143	1.01	2.26	0.65	2.91
	2	0.048	0.16	1.34	0.13	1.47
	5	0.341	0.57	1.63	0.64	2.27
	6	0.318	0.55	1.76	0.66	2.42
	7	0.137	0.18	...	...	1.33
	10	0.133	0.22	...	...	1.50
	15	0.207	0.98	...	...	0.88
	16	....	0.20	...	...	4.15
	18	0.160	0.47	...	...	1.44
	Average,	0.165	0.48	1.75	0.52	2.04
	Highest,	0.341	1.01	2.26	0.66	4.15
	Lowest,	0.048	0.16	1.34	0.13	0.88
Soft, porous or shaly stone, weathering rapidly, mostly blue.	3	2.120	2.37	7.73	10.19	17.92
	4	0.743	1.89	6.23	1.91	8.14
	8	0.952	1.90	17.43	7.64	25.07
	9	0.948	1.68	17.42	8.24	25.66
	11	0.666	0.96	4.20	4.08	8.28
	12	0.843	4.62	...	...	2.59
	13	0.710	6.24	...	...	2.06
	14	1.139	9.10	...	...	2.10
	17	2.044	4.52	12.53	10.23	22.76
	Average,	1.129	3.70	10.92	7.05	12.73
	Highest,	2.120	9.10	17.43	10.23	25.66
	Lowest,	0.666	0.96	4.20	1.91	2.06

A study of these results shows that the soft, blue, rapidly weathering limestones are characterized by the presence of high percentages of easily oxidizable matter and phosphates, accompanied in the shaly kinds by a high percentage of insoluble matter containing a large proportion of clay. In three instances there is

some appearance of a deviation from this rule. Sample No. 1 was selected as being very hard and apparently resistant to weathering, nevertheless it contains 1 per cent. of phosphoric anhydride, which is more than the average for good limestone. However, the "oxygen consumed" is not large. In samples 5 and 6, taken from a road in process of construction, the material of which was considered very good, the "oxygen consumed," while not excessive, is distinctly larger than in most of the selected gray rock, and the phosphoric acid is over 0.5 per cent., or slightly above the average. However, the uniform character of this stone is shown by the close agreement betwen the figures obtained from the selected piece, No. 5, and the average sample, No. 6. On this account the favorable opinion as to its quality may be considered to have been confirmed by this test.

CONCLUSION.

The conclusion would seem justified that the limestone which consumes much more than 0.3 per cent. of oxygen and at the same time contains as much as .1 per cent. of phosphoric acid, more especially if it contains also several per cent. of clay, will disintegrate rapidly upon exposure to air and moisture and will be undesirable for road building or other exposed construction.

While this method of analysis has not been tried upon other rocks than the Trenton limestone, it is probably of much more general application, especially that part of it which takes into account easily oxidizable constituents of rocks.

The writer is indebted to Mr. S. D. Averitt of this laboratory for assistance in the determinations of phosphoric acid and sand and the weighing of the total insoluble matter.

KENTUCKY AGRICULTURAL EXPERIMENT STATION,
LEXINGTON, KY., September 30, 1902.

[CONTRIBUTIONS FROM THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY.]

THE DETERMINATION OF ATMOSPHERIC CARBON DIOXIDE BY THE WALKER METHOD.

BY A. G. WOODMAN.

Received October 30, 1902.

DETERMINATIONS of carbon dioxide in atmospheric air or in the air of rooms, where results must be obtained with a considerable degree of accuracy, are usually made by the well-known

Pettenkofer method in some form or other. While this method is convenient and for a long time has been the favorite, it is now quite generally recognized that it contains inherent sources of error which can be obviated only by the use of complicated apparatus and extreme skill in manipulation. That the method can be employed to obtain results of the highest degree of accuracy, has been shown by Letts and Blake[1] in an exhaustive study of the question. The refinements found necessary, however, place their modification out of consideration for ordinary use. A method which is comparatively simple and at the same time accurate has been proposed by Walker.[2] This method may be briefly outlined as follows:

To a definite volume of air, usually 1 to 2 liters, is added a measured amount of standard barium hydroxide, care being taken to avoid contact of the solution with the air. After the absorption of the carbon dioxide, the solution is filtered under reduced pressure through asbestos and the clear barium hydroxide received into a known excess of standard hydrochloric acid. The absorption vessel is rinsed out with water free from carbon dioxide. The excess of acid is then determined by titration with barium hydroxide.

The principal errors of the Pettenkofer method in its usual modifications, *viz.*, contact of the absorbing solution with the carbon dioxide of the air or the exhaled breath, action of the caustic alkali on the glass of the container, and the presence of small amounts of the precipitated barium carbonate, are thus avoided.

The work which has been carried out has been mainly the determination of most suitable conditions, such as the necessary time for absorption, the most suitable filtering media, etc. A series of tests on air free from carbon dioxide and on mixtures of known amounts covering a wider range than those described by Walker, has also been made. It will be unnecessary to detail all the preliminary experimental work made to acquire familiarity with the apparatus and facility in manipulation. Much work which was found later to be of little value will be omitted entirely from the discussion. The analytical work has been of necessity

[1] *Proc. Royal Dublin Soc.*, **9**, 107 (1900).
[2] *J. Chem. Soc.*, **77**, 1110 (1900).

carried on with considerable interruption and has extended over some time.

REAGENTS AND APPARATUS.

The standard solutions used have been N/50 hydrochloric acid, and barium hydroxide, approximately N/100, its exact strength relative to the acid being found daily by titration. It was found advantageous to use solutions of this strength, somewhat more dilute than those recommended by Walker, on account of the increased accuracy with air nearly free from carbon dioxide. The decreased range of usefulness is readily compensated by the employment of smaller samples of the impure air.

The preparation of the acid requires no special comment, it being standardized by gravimetric determinations as silver chloride and preserved in a hard glass bottle in the usual manner. The barium hydroxide, which was made up in quantities of 8 liters at a time, was preserved with especial care. The hard glass bottle containing it, placed on a high shelf so that the measuring apparatus could be filled directly by gravity, was heavily coated on the inside with barium carbonate. This was found as efficient as the paraffin used by Letts and Blake which seemed to have a tendency to flake off with changes in temperature. The bottle was closed by a rubber stopper with two holes, one of which carried the siphon tube dipping to the bottom of the bottle and supplying the measuring burette, while the other carried a fairly large glass T (Fig .1). From one-half the horizontal arm of this projected a glass tube carrying the device for protecting the solution. This device is shown drawn on a somewhat larger scale in the same sketch. The horizontal tube entered the T-tube far enough to support the apparatus. Connection was made by a closely fitting rubber tube. The longer tube, reaching nearly to the bottom of the test-tube, carried a fairly good sized "calcium chloride tube" which contained soda-lime, enclosed in the usual manner by plugs of cotton. The test-tube contained 5 to 10 cc. of dilute (about N/50) caustic potash colored with phenolphthalein, the whole serving to indicate the efficiency of the soda-lime. From the other end of the horizontal arm of the T projected in the same way a long tube bent at right angles fitting by a rubber stopper into the top of the burette, thus making the whole a closed system,

much after the manner of Blochmann.[1] Any air entering the

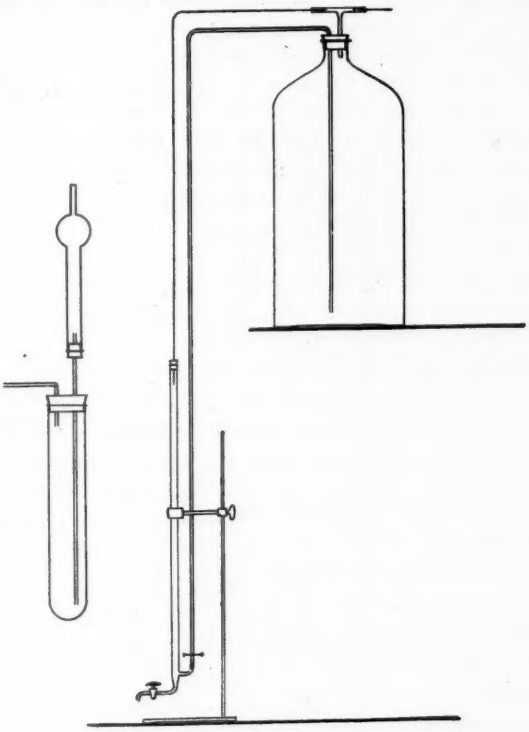


Fig. 1.

bottle when the solution is drawn from the burette or when the burette is filled again must have come through the protecting apparatus. This will be found efficient, if care is taken in the selection or preparation of the soda-lime.[2]

The burette used for the barium hydroxide was a glass-stoppered one, differing somewhat from the ordinary form. The lower portion below the graduations was narrowed and bent at right angles. This horizontal part was fitted with an ordinary glass stop-cock. This gave no trouble when kept well vaselined.

[1] *Ann. Chem.* (Liebig), **237**, 39 (1887).

[2] Directions for preparing a good quality of soda-lime are given by Benedict and Turner, this Journal, **21**, 396 (1899).

The tip of the burette was kept covered with a little rubber cap when not in use to prevent clogging from the formation of carbonate. The apparatus could easily be arranged with a special pipette for the delivery of a definite charge of baryta solution but this was not considered worth while for the purpose of testing the method. It was not found necessary to coat the inside of the tubes or the measuring apparatus with paraffin. The solution was always drawn from the burette and replaced by fresh if it had stood for any time. The apparatus as described was found to be remarkably efficient for the preservation of barium hydroxide. While determinations of the strength of the solution by titration against the hydrochloric acid were made every day, it was found as a matter of fact that the solution underwent no appreciable change during a month or so.

The bottles used for the collection of samples were of hard glass, some of 2-liters capacity, others of 1-liter, the exact volume being determined in each case to a cubic centimeter. Some of the bottles were fitted with glass tubes and stop-cocks as described by Walker; in others the stop-cock was replaced by a bit of rubber tubing and a Mohr pinch-cock which answers the purpose quite well though not so conveniently as the glass stop-cock. The bottles were used both plain and coated with paraffin.

The apparatus used for filtering off the barium carbonate, being made from material at hand, differed somewhat from that recommended by Walker. It may therefore need a word of explanation.

To the base of a ring-stand was firmly clamped an ordinary filter-bottle of about 250 cc. capacity closed by a rubber stopper with two holes. Through one of these passed a tube leading to the suction pump, through the other the tube of a Gooch filtering funnel, the upper part of which was cut off so that the remainder above the constriction was about an inch long. The tip projecting into the bottle was bent so that the liquid should flow down the side and not spatter. A rather close coil of stout platinum wire placed above the narrow portion served as a support for the asbestos filter or could be removed if it was desired to use cotton instead. In the upper part of the tube was tightly fitted a rubber stopper through which passed a narrow glass tube extending to within one-eighth inch of the asbestos layer and provided above

the stopper with a stop-cock. Connection was made with the

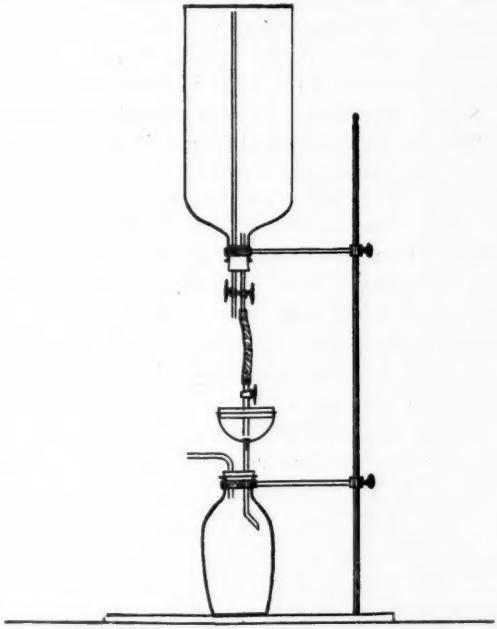


Fig. 2.

short tube of the inverted bottle by means of a rubber tube.

All rubber stoppers and connections with which the solutions could possibly come in contact were cleaned by boiling in a 5 per cent. potash solution, washed, and boiled in dilute bichromate and sulphuric acid mixture, rubbed thoroughly and washed until free from acid.

NOTES ON THE PROCEDURE.

The procedure adopted follows in its general outlines that of Walker but since it was found at an early stage of the work that success depended on a close observance of details in manipulation it might be well to mention the precautions found useful.

Collection of Samples.—With such small bottles, this is an easy matter. Any method may be used which secures a complete exchange of the air and prevents contamination with the breath.

It is better for this reason to draw the air out of the bottle than to force it in. For the present purpose, samples for comparison were collected by aspirating the air at a rapid rate through several bottles connected tandem, the air entering through the longer tube and leaving by the shorter one so as to sweep the bottle out completely. The air was drawn through usually for fifteen to thirty minutes, then the bottles allowed to remain connected for a time that the air might be equally distributed. No samples were collected at a temperature higher than that at the time of analysis and they were always allowed to come to the higher temperature of the laboratory so that there was always an outward pressure when the bottle was opened. It is, of course, unnecessary to use dry bottles for collecting the samples.

Absorption of the Carbon Dioxide.—It was found best instead of trying to force the alkali solution entirely below the level of the stop-cock by squeezing the rubber tip, to pinch it and then insert a bit of glass rod about an inch long as a plug to keep out the air. The absorption was usually carried on for thirty minutes.

Filtering off the Barium Carbonate.—25 cc. of the hydrochloric acid was used and the bottle was rinsed with 100-150 cc. of prepared "wash water"—made as suggested by Walker, by adding 1 cc. of a 10 per cent. barium chloride solution and 3 drops of phenolphthaleïn, then titrating with barium hydroxide to a faint permanent pink. Rinsing three times, using 25-30 cc. of wash water each time, was generally sufficient. One advantage of paraffined bottles is that they drain more completely and hence the washing is more readily performed. The preparation of this wash water was usually carried out during the absorption and the water kept in stoppered flasks. Some of the water should also be used to wash down the filter tube.

Equally good results were obtained by using 100 cc. of distilled water which had had air free from carbon dioxide passed through it in a fairly rapid stream for two hours and then been preserved out of contact with the air. This was usually done on a considerable quantity which was kept in a hard glass bottle and drawn off through a siphon tube as required for use.

The Titration.—The acid solution was transferred from the filter bottle to a 6-inch porcelain dish for titration. Barium hydroxide was added to the production of a distinct pink color,

the solution then returned to the bottle and finally poured again into the dish. One or two drops of the alkali solution usually sufficed to finish the titration.

EXPERIMENTAL.

Standardization of the Barium Hydroxide.—This was the first problem that presented itself. The natural method would seem to be titration directly against the hydrochloric acid, using the indicator used in the actual determination; but since "neutralized water," that is, distilled water in which the dissolved carbon dioxide had been neutralized with baryta, was to be used in the determination, it seemed on the other hand, that the standardization should be carried out under similar conditions as regards dilution. Again, since barium chloride has been added to the wash water to assist in the separation of the barium carbonate and it has passed through a filter, the carbon dioxide may be considered removed. Why, then, should not equally good results be obtained, with less trouble, by determining the amount of carbon dioxide in a given volume of water and applying a correction for the amount of wash water used? Still another method was by the use of "purified water," by which is meant distilled water with the carbon dioxide removed as previously described.

These four methods, then, have been tried: (*a*) Direct standardization; (*b*) using 150 cc. of "neutralized water" to dilute the hydrochloric acid solution; (*c*) applying a correction for the amount of carbon dioxide in the diluent water; (*d*) using 100 cc. of "purified water."

The results are given in Table I, the value calculated being that of the barium hydroxide in terms of the standard acid.

TABLE I.—METHODS OF STANDARDIZATION.

a.	*b.*	*c.*	*d.*
0.5175	0.5225	0.4855	.....
0.5147	0.5170	.....	.....
0.4832	.....	.....	0.4829
0.4832	.....	.....	0.4831
0.4796	.....	.....	0.4794
0.4798	.....	.....	0.4803
0.4924	0.5048	.....	0.4928
0.4948	0.5077	0.4808	0.4945

The values obtained with purified water and by direct standardization were nearly the same and are undoubtedly the correct

ones. Distilled water gave values which were too low, even when a correction was made for the carbon dioxide that it contained. The results with neutralized water, on the other hand, which might be expected to agree with those for purified water, were invariably high. This is probably due to the barium carbonate which has not been removed, since experiments made with a small flask exhausted of its air and fitted with stop-cocks and the filtering arrangement gave results identical with the direct standardization.

The method of standardization finally adopted was either the direct method or the use of 100 cc. of purified water, the bottle being rinsed out with 150 cc. of neutralized water, for which no allowance was made. That is to say, none was poured directly into the filter bottle but all that was used passed through the filter.

The Filtering Medium.—Tests were made using asbestos as the filtering medium and also using cotton. It was found rather more convenient to use a bit of absorbent cotton packed into the stem of the funnel tube in place of the platinum coil. A comparison of the two showed that for ordinary work either medium could be employed but that the cotton gave slightly higher results, as might be expected from the results published by Reiset[1] on the filtration of baryta water through paper.

TABLE II.—FILTERING MEDIA.

Source of air.	Filter.	Time. Minutes.	CO^2 in 10,000.
Outdoors	Cotton	30	3.26
"	Asbestos	30	3.18
Room	Cotton	30	4.05
"	Asbestos	30	4.01
"	Cotton	30	4.10
"	Asbestos	30	3.93
"	Cotton	30	3.99
"	Asbestos	30	4.01

Time Necessary for Absorption.—It is possible to carry out the absorption of the carbon dioxide in fifteen minutes, as Walker states, by agitating the bottle almost constantly. In most cases, however, it would be better to continue the absorption for a little longer time, say for twenty to thirty minutes. A longer time than this is unnecessary and in the case of bottles which are not paraffined it is undesirable.

[1] *Ann. chim. phys.*, [5], **26**, 155 (1882).

TABLE III.—TIME NECESSARY FOR ABSORPTION.

Source of sample.	Time of shaking. Minutes.	CO_2 in 10,000.
Room	15	3.89
"	30	3.99
"	60	3.95
"	60	3.93

Action of the Alkali on the Glass of the Bottle.—The tests which were made confirmed Walker's conclusion that in the short time necessary for absorption the solvent action of the alkali on the glass is negligible.

TABLE IV.—ACTION OF THE ALKALI ON THE GLASS.

Source of sample.	Paraffined bottle?	Time. Minutes.	CO_2 in 10,000.
Room	No	30	3.68
"	"	30	3.63
"	Yes	30	3.75
"	"	30	3.78
"	No	30	4.84
"	Yes	30	4.78
"	"	30	4.81

Tests on Air Free from Carbon Dioxide and on Known Mixtures.—To obtain a rigid test of the method, determinations were made on air free from carbon dioxide and on similar samples to which a known amount of the gas had been added. The blank determinations were made both on the vacuous bottles from a previous determination and on samples in which air free from carbon dioxide was drawn through the bottles until the original air was entirely displaced. This was determined by passing the air from the bottle through a saturated solution of baryta and in no case was the sample used if the clear solution showed any turbidity when the air was drawn through it at a rapid rate for twenty minutes.

In the tests on known amounts of carbon dioxide, the vacuous bottles were also employed. The carbon dioxide, which was generated by heating magnesium carbonate, was measured over mercury in capillary tubes and added through the shorter tube of the bottle.

TABLE V.—TESTS ON AIR FREE FROM CARBON DIOXIDE.

Filter.	Wash water used.	Standardization.	CO_2 in 10,000.
Cotton	Neutralized	Direct	—0.14
"	Purified	"	0.06
"	Neutralized	"	0 00
"	Purified	"	0.18
"	"	Purified water	0.01
"	Neutralized	Direct	0.07
"	Purified	"	—0.02
"	Neutralized	"	—0.06
None	"	"	—0.01
Cotton	"	"	0.01
"	"	"	—0.02
"	"	"	0.01
Asbestos	"	"	—0.02
"	Purified	"	—0.01
"	Neutralized	"	0.01
"	Purified	"	0.00
"	"	"	0.01
"	"	"	0.01
"	Neutralized	"	0.03
"	"	"	—0.07
"	"	"	0.05
"	"	"	—0.01
"	"	"	0.03

TABLE VI.—TESTS WITH KNOWN AMOUNTS OF CARBON DIOXIDE.

Cc. added.	Temperature.	Bar. Inches.	Cc. N. T. P.	Volume found.
0.852	25.8°	29.85	0.752	0.744
0.841	27.0	30.07	0.742	0.715
1.33	25.0	29.97	1.182	1.182
1.28	24.8	29.96	1.139	1.16
2.011	25.0	29.92	1.784	1.802
1.23	25.3	29.92	1.090	1.075
2.221	25.4	29.92	1.967	2.01
2.158	25.3	29.89	1.972	1.945
1.37	21.2	30.24	1.285	1.286
1.325	21.8	30.24	1.240	1.273
2.074	21.8	30.23	1.941	1.922
1.877	23.0	30.18	1.746	1.708
0.878	23.6	30.18	0.815	0.791
0.996	23.6	30.18	0.924	0.919
1.057	22.6	....	0.990	0.996

CONCLUSIONS.

The results obtained confirm Walker's statement that the method is accurate under ordinary circumstances to 0.1 part in

10,000. With careful work and attention to details it should be accurate to a much greater degree than this, certainly to 0.03 part. It can hardly be said, however, that amounts of carbon dioxide varying from 0 to 40 parts in 10,000, can be determined without modification of the method. The barium hydroxide must always be present in considerable excess, a condition which is most readily attained by the use of a smaller sample of bad air. With a little practice, the method was found to be rapid and easy of execution and preferable to the Pettenkofer method.

BOSTON, MASS.,
October 28, 1902.

LIQUID BATHS FOR MELTING-POINT DETERMINATIONS.

BY HEYWARD SCUDDER.

Received November 28, 1902.

A MIXTURE prepared by boiling together for five minutes seven parts by weight of sulphuric acid (sp. gr. 1.84) and three parts by weight of potassium sulphate remains a transparent liquid at ordinary temperatures and can be heated up to 325° without boiling. If the proportions are changed to six parts by weight of acid and four parts of the sulphate the mixture forms a soft mass at ordinary temperatures (though after boiling and then cooling down it will usually remain liquid for half an hour or more) melting from 60°-100° and boiling above 365°. Acid potassium sulphate can be used instead of potassium sulphate. In this case the amount should be calculated to give the same ratio of potassium sulphate to sulphuric acid.

These mixtures are self-clearing and remain permanently white (turning slightly yellowish at about 230°) unless much organic matter gets in. They can be cleared, if brown, by boiling with a few drops of concentrated nitric acid or with a small crystal of potassium nitrate. The vapor is so slightly acid that the capillary can always be fastened to the thermometer by a rubber band, provided the band is 1 to 2 cm. above the surface of the bath. Platinum wire need never be used. In preparing the bath, after the potassium sulphate has melted the two layers should be mixed or explosive boiling may occur.

Most melting-points given accurately are below 325°. The first mixture is therefore suitable for all ordinary purposes. It

does not have to be renewed frequently as does the ordinary sulphuric acid bath nor does it become permanently discolored as does paraffin after short use, even though prepared by distillation under diminished pressure.

If the bath has solidified (which happens sometimes under unknown conditions though very rarely), boiling for a minute or two will bring it back to its original condition. If it has not been used for a number of weeks, it should be boiled for a minute or two before using for temperatures above 300°.

For temperatures from 360° to 600° Mr. Booth, working under the direction of Dr. Mulliken of this laboratory, has found that the most satisfactory bath is fused zinc chloride. This melts to a clear transparent liquid at about 250°. After use it must be poured out on a tile while liquid, since it expands on solidification and will crack any flask or beaker in which it is allowed to grow cold. It can be cleared from organic impurities by heating with a small crystal of potassium nitrate. Unless the zinc chloride used is pure, the bath will gradually become opaque after a short time and can not be made transparent again.

The temperatures given here are uncorrected. They were obtained in a melting-point apparatus made by inserting a test-tube in a round-bottomed flask (150-250 cc.). The bottom of the tube is about 1 cm. from the bottom of the flask. The bath is placed both in the test-tube and in the flask. In this apparatus fresh sulphuric acid (sp. gr. 1.84) can be used up to 280°-300°. In using the sulphate mixtures, if the upper part of the tube becomes cloudy from a film of solid, it can be cleared by boiling with a little concentrated nitric acid. In using such an apparatus it is not safe to heat it much above the temperatures given here for the various baths since the boiling is apt to start very violently. It is safe to heat it till large bubbles begin to rise moderately frequently.

When these baths are used in open beakers, it is not possible with sulphuric acid or the sulphate mixtures to obtain temperatures as high as those previously mentioned, without having disagreeable amounts of acid vapor given off. The zinc chloride bath can be used in a beaker up to about 600°.

The sulphate mixtures seem to contain some compound in a persistent state of supersaturation. Although possessed of considerable oxidizing power when hot, it is a curious fact that they

are markedly less caustic than hot concentrated sulphuric acid when dropped on the skin.

MASSACHUSETTS INSTITUTE OF TECHNOLOGY,
November, 1902.

THE PREVENTION OF BUMPING.

BY HEYWARD SCUDDER.

Received November 28, 1902.

A SINGLE glass capillary tube when used according to the following directions will stop most cases of bumping that occur in ordinary laboratory work. The method is simple, effective and introduces into the liquid no foreign substance except glass and one small bubble of air. In order to carry it out successfully the following details of procedure must be carefully observed.

The origin of the use of a capillary is obscure. The earliest published reference that I have found is by Gernez.[1] Since these references are only incidental and therefore difficult to find, it is quite possible that there may be an earlier one. I have tried all the methods published (most of which are only for special cases), and have found none so simple or of such wide application as the one presented here.

The capillary is made by drawing out a piece of glass tubing until the internal diameter is about 0.5 to 1 millimeter. A seal is then made by holding the tube horizontally in the edge of the flame of a Bunsen burner, until the walls have melted together. The tube is bent, if necessary, or held horizontally till cold. For most purposes the seal should be about 1 cm. from the open end of the tube. The tube is cut off at the desired length and the other end sealed to prevent the entrance of liquid. When cold, the tube is placed open end down in the liquid to be boiled. The open end should rest on the bottom of the vessel containing the liquid and should remain there during use. When liquids of high specific gravity are being boiled, it is necessary, therefore, to have the capillary so heavy that it will not be thrown off the bottom. This weight can be obtained by drawing out the tube from which the capillary is made only near the seal, or by using a very thick walled tube.

In a general way the theory of the action of such a tube is that

[1] *Compt. Rend.*, **86**, 472.

when heated the air in the capillary expands and passes through the liquid in bubbles. The vapor of the liquid gradually replaces the air and the stream of bubbles is continuous as long as the temperature around the capillary is at the boiling-point of the liquid. This constant bubbling prevents superheating and consequent explosive boiling. It is apparent that the size of the bubble will depend chiefly on the width of the capillary. This should vary with the nature of the liquid. For liquids of low boiling-point or for frothing liquids a narrow capillary is best, while for heavy liquids a wider capillary (even as wide as 5 mm. internal diameter) is more suitable.

When boiling with a return condenser, the seal of the capillary *must* be below the surface of the liquid. If the seal is above the surface, cold drops falling back from the condenser will strike the capillary and cause condensation of the vapor inside it, thus stopping the stream of bubbles. To prevent displacement, the capillary should be of such a length that the upper end reaches nearly to the top of the neck of the flask. When the liquid is in a thin broad layer the capillary should be bent at the seal so as to be parallel or nearly parallel to the bottom of the flask. In boiling liquids in a test-tube, care must be taken that the heat is applied at the bottom of the tube. When a solid is being dissolved, or when in the course of a reaction a solid is being precipitated out of solution, the capillary should be examined from time to time to see that the end has not become clogged.

The capillary is useless, if completely filled. Therefore it must be cold and empty when placed in the liquid. Care should be taken (especially in the case of liquids that usually bump badly) to protect the flame from drafts, so that the temperature of the liquid shall not temporarily fall below the boiling-point, allowing the capillary to fill.

Other minor changes and precautions may be advisable at times, but it will be found that they depend on the following principles. The capillary must never be allowed to become filled with liquid. The greater the amount of air there is to drive out (depending on the width of the capillary and the distance from the seal to the open end), the longer will it take to get a rapid stream of bubbles of vapor of the liquid. The greater the distance from the seal to the open end, the longer will it take to fill the capillary on cooling.

This method has been in successful use in these laboratories for nearly a year. By its use it is possible to saponify esters by boiling with a 50 per cent. solution of potassium hydroxide (using a return condenser) or to boil concentrated sulphuric acid in a test-tube, without any bumping. Only two cases have been met with in which bumping persisted after the capillary was introduced. Both were reactions carried out with a return condenser. Although the bumping continued, it was so greatly lessened that the liquid was not thrown out of the upper end of the condenser and there was no danger of having the flask broken.

MASSACHUSETTS INSTITUTE OF TECHNOLOGY,
November, 1902.

[CONTRIBUTIONS FROM THE LABORATORIES OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY.]

THE EQUIVALENT CONDUCTIVITY OF THE HYDROGEN ION DERIVED FROM TRANSFERENCE EXPERIMENTS WITH HYDROCHLORIC ACID.

BY A. A. NOYES.

Received November 17, 1902.

(SECOND PAPER.)

IN a previous communication[1] bearing the same title made by A. A. Noyes and G. V. Sammet three series of determinations of the transference-numbers for $^1/_{60}$ molar hydrochloric acid, at 10°, 20°, and 30°, respectively, were presented, from which by combination with the fairly accurately known values for the conductivity of the chlorine ion, the following ones for that of the hydrogen ion were obtained.

t.	10°.	18°.	20°.	25°.	30°.
Λ	288.7	329.8	340.0	364.9	389.1

These values are 4 to 6 per cent. higher than those derived by Ostwald and Kohlrausch through a consideration of the change of conductivity of strong acids with the dilution. It was not considered possible that this divergence could arise from experimental errors in the transference determinations; but it was suggested that it might be due, at any rate in part, to a difference in the transference-numbers of the acid at extreme dilution and at the investigated dilution of 60 liters. To test this possibility, a new series of determinations has been made at 20° with an approxi-

[1] This Journal, **24**, 944 (1902).

mately $^1/_{180}$ molar acid; and it is the purpose of this article to communicate the results. In this investigation I have been ably assisted by Mr. Raymond Haskell.

The method employed was substantially identical with that described in the previous article. The acid used was prepared from pure salt and sulphuric acid, washed with water, absorbed in a little pure water, and diluted with water having a conductivity of 1.5×10^{-6} reciprocal ohms. Three separate solutions, numbered 10, 11 and 12 in the table, were employed. These yielded respectively 0.7870, 0.7815, and 0.8240 milligram AgCl per gram of solution.

The data are given in detail in the following table, which is arranged like those previously published. The headings are for the most part self-explanatory. The content is always expressed in milligrams AgCl per gram of solution. The silver precipitated in the voltameters is also given in milligrams. The "transference-numbers" of the table are the actual values for the anion multiplied by 1000. The letters in the third column have the following significance: K = cathode portion; A = anode portion; M_K and M_A the middle portions adjoining these, respectively; M, the middle portion of all, lying between the last two.

$^1/_{180}$-MOLAR HCL AT 20°.

Expt. No.	Solution No.	Portion.	Weight of portion. Grams.	Initial content.	Final content.	Change in content.	Total change in content.	Silver in voltameters.	Transference number.
33	10	K	346.42	272.6	223.7	−48.9	−48.9	217.2	169.4
		M_K	210.26	165.4	165.2	− 0.2	.....	217.4	....
		M	177.44	139.6	138.1	− 1.5	.....	217.1	....
34	11	K	343.00	268.1	230.7	−37.4	−37.4	168.4	166.9
		M_K	142.68	111.5	111.7	+ 0.2	.....	168.7	....
		M	163.00	127.4	127.1	− 0.3	.....	168.7	....
35	11	K	340.56	266.2	229.3	−36.9	−36.9	167.1	166.3
		M_K	160.37	125.3	125.5	+ 0.2	.....	167.2	....
		M	168.81	131.9	130.8	− 1.1	.....	167.4	....
36	11	K	356.44	278.6	237.5	−41.1	−41.1	186.1	166.4
		M_K	160.64	125.5	125.5	± 0.0	.....	186.0	....
		M	183.78	143.6	140.9	− 2.7	.....	185.8	...
37	11	K	349.28	273.0	234.8	−38.2	−38.2	172.0	167.2
		M_K	160.89	125.7	125.5	− 0.2	.....	171.8	....
		M	187.42	146.5	142.5	− 4.0	.....	172.1	....
		A	487.95	381.4	424.1	+42.7	+38.7	....	169.3

Expt. No	Solution No.	Portion.	Weight of portion. Grams.	Initial content.	Final content.	Change in content.	Total change in content.	Silver in voltameters.	Transference number.
38	12	K	319.12	263.0	221.8	−41.2	−41.2	185.0	167.7
		M_K	162.63	134.0	133.7	− 0.3	.....	185.0	....
		M	177.87	146.6	142.2	− 4.4	.....	185.1	....
		A	451.47	372.0	417.4	+45.4	+41.0	....	166.8
39	12	K	323.36	266.5	232.4	−34.1	−34.1	155.8	164.6
		M_K	136.82	112.7	112.6	− 0.1	.....	156.0	....
		M	169.80	139.9	138.3	− 1.6	.....	156.0	....
		A	451.46	372.0	410.9	+38.9	+37.3	....	180.0
40	12	K	305.85	252.0	210.1	−41.9	−41.9	188.0	167.7
		M_K	156.41	128.9	128.6	− 0.3	.....	188.3	....
		M	181.01	149.2	143.3	− 5.9	.....	188.1	....
		A	431.19	355.3	403.3	+48.0	+42.1	....	168.5
41	12	K	306.64	252.7	216 9	−35.8	−35.8	167.9	160.5
		M_K	156.91	129.3	129.5	+ 0.2	.....	168.0	....
		M	177.42	146.2	143.4	− 2.8	.....	167.9	....
		A	445.75	367.3	407.1	+39.8	+37.0	....	165.9
42	12	K	309.99	255.4	219.2	−36.2	−36.2	163.4	166.4
		M_K	162.39	133.8	133.6	− 0.2	.....	163.9	....
		M	172.73	142.3	139.3	− 3.0	.....	163.8	....
		A	453.88	374.0	414.2	+40.2	+37.2	...	170.9

The transference numbers are summarized in the following table. The values marked with an asterisk were omitted in the calculation of the mean.

$^1/_{180}$-MOLAR HCL AT 20°.

Expt. No.	Cathode.	Anode.
33	169.4	....
34	166.9	....
35	166.3	....
36	166.4	....
37	167.2	169.3
38	167.7	166.8
39	164.6	180.0*
40	167.7	168.5
41	160.5*	165.9
42	166.4	170.9
	Mean, 167.0	168.3
	a.d., 0.9	1.5
	A.D., 0.3	0.7
	Final mean, 167.1	
	A.D., 0.3	

The agreement of the cathode values among themselves is nearly as close as it was with the $^1/_{60}$ molar solution (where the a.d. was 0.8). The change in content of the adjoining portion M_K is also very small, mostly 0.2 mg. or less, and has opposite signs in different experiments. Even if this were added to the change in the cathode portion, it would increase the mean of the transference values by only 0.2 per cent. The anode values are much more discordant than the cathode values, owing to the more difficult manipulation involved in the preparation of the anode portion for analysis.[1] Nevertheless, the agreement of their mean with that of the cathode values within 0.8 per cent. is a confirmation of the substantial accuracy of the latter.

The final mean derived from the earlier determinations at 20° with $^1/_{60}$ molar solutions was 167.43 (A.D., 0.25). This agrees with the final mean of the present determinations (167.1; A.D., 0.3) at 20° with $^1/_{180}$ molar solutions within 0.25 per cent. (and within the limits of the sum of the A.D.'s). Hence it is justifiable to conclude that the transference-number of hydrochloric acid does not change appreciably with increase of the dilution after that of 60 liters is reached. The equivalent conductivities of the hydrogen ion derived in the previous article and summarized at the beginning of this one were therefore not vitiated by this assumption, which was made in their deduction.

The deviation between these values and those derived by extrapolation from the conductivities of acids still requires explanation. Whether it can be due to error in the estimate of the effect of the impurities of the water on the conductivities at great dilution could probably be determined through an investigation of that effect. Such an investigation will be undertaken in these laboratories.

BOSTON, November, 1902.

[1] In the first four experiments the anode results had to be rejected, owing to the use in the process of a large and indefinite amount of ammonium hydroxide, which was afterwards found to contain an appreciable quantity of chloride. In the later experiments a smaller and definite quantity of ammonia was used, and its chlorine-content determined and subtracted.

ON THE COLORIMETRIC DETERMINATION OF SMALL QUANTITIES OF PHOSPHORIC ACID AND OF SILICA.

By F. P. Veitch.

Received November 23, 1902.

In some of the field work of this bureau the analysis of drainage waters and of water extracts of soil is required daily. For this purpose the usual gravimetric processes are deemed impracticable on account of the time required, and it has been necessary to use more rapid volumetric, colorimetric, and photometric methods.

The writer suggested, and in the spring and early summer of the past year made an examination of, some known rapid colorimetric methods for the determination of phosphoric acid and of silica in these soil solutions. Incidentally, as the presence of iron in considerable amounts introduces errors in the determination of phosphoric acid, the rapid methods for the detection and estimation of minute quantities of iron have received some attention. As these latter methods have been thoroughly worked out and are quite well known, but passing reference need be made to them here.

For the estimation of phosphoric acid, the method described by Lepiere[1] and later studied in more detail by Woodman and Cayvan[2] promised to be the most rapid and to present the fewest difficulties in its manipulation.

For the adaptation of this method to the analysis of soil solutions, the influence of other compounds, both organic and inorganic, must be eliminated or determined. It was found that turbidity, organic matter where it produced a colored solution, ammonia salts in large amounts, iron salts in small amounts, dissolved silica and filter-paper introduce errors which are not negligible.

REMOVAL OF SUSPENDED MATTER.

Turbidity may be removed by filtering through a Chamberland filter, which of course removes some of the phosphoric acid from the first runnings (see Table VIII). It may also be quite largely, sometimes completely, removed by evaporation to dryness

[1] *Bull. Soc. Chim.*, **15**, 1213 (1896).

[2] This Journal, **23**, 96.

The agreement of the cathode values among themselves is nearly as close as it was with the $^1/_{60}$ molar solution (where the a.d. was 0.8). The change in content of the adjoining portion M_K is also very small, mostly 0.2 mg. or less, and has opposite signs in different experiments. Even if this were added to the change in the cathode portion, it would increase the mean of the transference values by only 0.2 per cent. The anode values are much more discordant than the cathode values, owing to the more difficult manipulation involved in the preparation of the anode portion for analysis.[1] Nevertheless, the agreement of their mean with that of the cathode values within 0.8 per cent. is a confirmation of the substantial accuracy of the latter.

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[1] *Bull. Soc. Chim.*, **15**, 1213 (1896).

[2] This Journal, **23**, 96.

and filtering; or it may be corrected for by matching the standard phosphomolybdate solution against the turbid solution and subtracting this reading from the final readings. None of these procedures is perfectly satisfactory, but nothing better has yet been devised. All have been used here, according to the difficulties presented. Where filtration will remove all suspended matter, this procedure is to be preferred, but as this cannot always be accomplished, the Chamberland filter or evaporation must be resorted to.

In the work about to be described the reagents were prepared as directed by Woodman and Cayvan[1] and were free from interfering substances. The same lot was used throughout the work, and all work was done at from 18°-22° C., the standard and the unknown solution being of course at sensibly the same temperature.

REMOVING ORGANIC MATTER.

Organic matter which colors the solution at all must be removed or it must be corrected for as above described, before reliable readings can be made. To accomplish this, two methods were tried: treatment with aqua regia, and ignition with magnesium nitrate. Several treatments with aqua regia were required to insure the destruction of all organic matter, after which the solutions were carried to dryness, taken up with water and 2 cc. nitric acid and compared in a reflecting colorimeter. The following readings were obtained:

TABLE I.

	Amount P_2O_5 added.	Amount P_2O_5 recovered.		Amount P_2O_5 added.	Amount P_2O_5 recovered.
	Parts per million.			Parts per million.	
1	1.0	1.0	4	5.0	4.3
2	2.0	1.1	5	7.0	6.1
3	3.5	2.4	6	9.0	7.1

We see that there is considerable loss of phosphoric acid from this concentrated aqua regia solution, a fact previously pointed out by Woodman and Cayvan.

Other phosphate solutions were then treated with magnesium nitrate free from silica, evaporated to dryness with nitric acid, and ignited in a porcelain dish until all carbon was burned off. The residue was then taken up with water and nitric acid, and compared with the standard solution.

[1] *Loc. cit.*

TABLE II.

	Amount P_2O_5 added.	Amount P_2O_5 recovered.		Amount P_2O_5 added.	Amount P_2O_5 recovered.
	Parts per million.			Parts per million.	
1	1.0	1.0	8	3.0	2.7
2	2.0	1.8	9	1.0	1.0
3	4.0	3.7	10	5.0	5.2
4	6.0	5.9	11	10.0	10.0
5	8.0	7.9			
6	9.0	9.2		Average loss,	0.06
7	10.0	9.9			

The loss here is quite small, being as a rule within the limit of error of the reading. From these experiments it appears that the organic matter may be satisfactorily removed without loss of sensible amounts of phosphoric acid by ignition with magnesium nitrate and subsequent evaporation with nitric acid.[1] It may be said, however, that when the color due to organic matter is not greater than 0.2 to 0.3 part per million, it is hardly worth while to remove the organic matter, as a correction may be made for it by reading the color due to organic matter against the standard, and correcting the final reading by the reading thus obtained.

The volatility of phosphoric acid upon evaporation of these water solutions is at first sight rather startling to analysts, and while there is not the slightest doubt that it does take place from solutions of phosphoric acid[2] and from disodium phosphate solutions, there appears to be no reason to think that it occurs from solutions containing sufficient bases to form the normal phosphates. In no case has the writer obtained a loss from solutions of this character. As phosphates dissociate readily, it seems possible that water extracts of soils may contain occasionally some free phosphoric acid or acid phosphates from which phosphoric acid is partly volatilized upon evaporation. That this does not take place in the presence of a large excess of base, even from acid solutions, is shown positively by the experiments with magnesium nitrate.

INFLUENCE OF THE PRESENCE OF OTHER SALTS.

Ammonia salts in considerable quantities decrease slightly the intensity of the color reaction. Ammonium nitrate added to the unknown solution at the rate of 0.04 gram per 50 cc. gave readings on 4 parts per million of standard of only 3 parts, which increased a little on standing, but the solution soon precipitated.

[1] Subsequent work has confirmed these results in every instance.

[2] It seems possible that this apparent loss may be due to the formation of pyrophosphoric acid.—EDITOR.

Ammonium chloride does not give a water-white solution always —has a tendency to be slightly opaque, and it also prevents the full development of the color. The figures obtained are given in the table.

TABLE III.—EFFECT OF AMMONIUM SALTS.

Parts per million NH_4NO_3.	Parts per million P_2O_5 added to NH_4NO_3 solution.	=	Parts per million P_2O_5 without NH_4NO_3.	Solution with NH_4NO_3 commenced to precipitate.
4000	1.0	=	0.7	not in 5 min.
4000	4.0	=	2.0	nearly as dark but precipitated too rapidly to be sure.
4000	4.0	=	3.0	nearly as dark but precipitated too rapidly to be sure.
800	4.0	=	3.3	precipitated in 50 min.
800	4.0	=	3.7	" " 75 "

Calcium nitrate, barium chloride, potassium nitrate, and aluminum sulphate, separately and together, were added to solutions at the rate of 0.25 gram of each salt to 50 cc. of solution. None of these except the aluminum sulphate affected the readings more than 0.1 part per million, or within the limit of error of readings. Aluminum sulphate in this quantity gave a dark, opaque solution which could not be matched satisfactorily against the standard.

It was found that iron salts in considerable quantities exerted a marked influence not only on the color of the solution itself, in the first instance, an influence which it was found could be corrected for by reading against the standard, but there is also a reaction between the iron salt and the molybdate, a reaction which appears to bear a relation to the amount of iron present, and which possibly may be used for the estimation of the iron in solution. As iron is present in many soil extracts, the reaction of iron with the molybdate solution required careful study in order to determine the amounts and conditions which would vitiate the phosphate readings. The results of the investigation of this point are given in Table IV. Unless otherwise stated, the two solutions were identical in all particulars except that one contained iron in the amounts given in the table. The iron salt was made from pure wire, the solution of which was evaporated to dryness several times to remove traces of silica and hydrochloric acid.

TABLE IV.—COLOR PRODUCED BY IRON SALTS WITH MOLYBDATE SOLUTION.

Preliminary Series.

Parts per million of Fe in solution.	Parts per million P_2O_5 to equal color of Fe solution before molybdate was added.	Parts per million P_2O_5 to equal color of Fe solution after molybdate was added to Fe solution.	Parts per million of P_2O_5 to equal color produced by adding 1 part per million P_2O_5 to Fe solution containing molybdate.
4000	3.0	6.5	...
2000	..	3.0	...
2000	0.6	2.5	...
2000	..	4.0	1.05
2000	..	3.1	0.95
2000	..	3.0	1.10
400	2.2	3.2	...
200	0.8	1.6	1.10
80	0.2	0.8	1.00
40	0.1	0.3	1.00
40	0.1	0.5	...
40	0.1	0.5	1.00

Final Series.

100	0.1	0.75 0.75 0.80
50	0.0	0.40 0.40 0.50
20	0.0	0.10 0.10
10	0.0	0.00 0.00
8	0.0	0.00 0.00
4	0.0	0.00 0.00
2	0.0	0.00 0.00

The presence of less than 20 parts of iron (Fe) per million of solution introduces no appreciable error in the determination, while as much as 50 parts per million vitiate the phosphate results, unless the amount of iron present is known and its reading subtracted from the total reading. As soil extracts seldom contain more than 0.1 to 5 parts per million of iron, further study of the influence of iron has been temporarily discontinued, but it is hoped to devote more attention to this point later. It is of course necessary, where the presence of considerable iron is indicated, to assure one's self that not more than 20 parts per million are present

before the reading can be accepted as representing phosphoric acid alone. This is quite readily ascertained by adding potassium sulphocyanide or ferrocyanide to the acidulated extract and matching the developed color against an iron standard.[1]

EFFECT OF VARYING THE AMOUNT OF NITRIC ACID PRESENT.

Woodman and Cayvan[2] found that the depth of color and the rapidity with which it developed depended to a certain extent on the amount of reagents present in the solution, and further state that the best results were obtained with 4 cc. of ammonium molybdate solution (50 grams of the salt per liter) and 2 cc. of nitric acid (sp. gr. 1.07) per 50 cc. of the solution to be examined.

It appeared advisable to make an experimental study of these points in order to obtain data on the allowable variations in amounts of added reagents. To this end solutions containing different amounts of nitric acid and also different amounts of standard phosphate solution were compared with solutions containing 2 cc. of nitric acid and 4 cc. of molybdate. The results follow:

TABLE V.—EFFECT OF VARYING THE QUANTITY OF NITRIC ACID ADDED.

HNO_3 Cc.	+ Na_2HPO_4 Cc.	+ Molybdate Cc.	= Na_2HPO_4 Cc.	+ HNO_3 Cc.	+ Molybdate. Cc.
1	1	4	0.83	2	4
2	1	4	1.04	2	4
3	1	4	1.10	2	4
4	1	4	1.15	2	4
5	1	4	1.24	2	4
6	1	4	0.98	2	4
7	1	4	0.97	2	4
8	1	4	0.88	2	4
10	1	4	0.84	2	4

The intensity of the color is sharply and regularly affected by the amount of nitric acid present, and it is of particular interest to note that there is a maximum point at which the color is most intense: with less acid or with more acid present the intensity of color is considerably reduced and it is evident that to obtain strictly comparable results the standard and the solution to be read must contain, in a given volume, sensibly the same amount of acid.

Possibly these results are also of interest in throwing light on the precipitation of ammonium phosphomolybdate and may ex-

[1] Sutton's "Volumetric Analysis," eighth edition, p. 245.
[2] *Loc. cit.*

plain the results sometimes obtained. It is a well-known fact that the color of the precipitate varies with the amount of acid present from a light lemon-yellow to a deep orange, and the speed with which the precipitate is formed also varies with the amount of nitric acid present. Under the best conditions this precipitation takes place rapidly and is complete; the supernatant fluid is practically as colorless as water, even when it contains a considerable amount of iron salt. On the other hand, under some other condition the precipitate forms slowly, is "muddy," filters and washes slowly, and shows a decided tendency to run through the filter, while the filtrate generally has a decided color, due apparently to the ammonium phosphomolybdate still in solution.

The above results show that the presence of 5 cc. of nitric acid (sp. gr. 1.07) per 50 cc. of solution gives the most intense color, and this amount has been adopted for this work. Whether or not this relation gives the optimum condition for the precipitation of ammonium phosphomolybdate, remains to be investigated.

EFFECT OF VARYING THE QUANTITY OF MOLYBDATE.

The effect of varying the quantity of molybdate was studied in the same way. The standard and the solution to be read were identical in all particulars except that in the standard the amount of molybdate present in 50 cc. was always 4 cc., while in the other solution the amount of molybdate varied.

TABLE VI.—EFFECT OF VARYING THE QUANTITY OF MOLYBDATE ADDED.

Molybdate Cc.	+ Na_2HPO_4 Cc.	+ HNO_3 Cc.	= Na_2HPO_4 Cc.	+ molybdate Cc.	+ HNO_3. Cc.
2	1	5	0.85	4	5
4	1	5	1.00	4	5
6	1	5	1.15	4	5
8	1	5	0.97	4	5
12	1	5	0.96	4	5

The results show considerable differences due to varying the amount of molybdate. These differences are not as great nor is the maximum point as well defined as with different amounts of nitric acid, and there seems to be no reason for changing the amount of molybdate adopted by Woodman and Cayvan as giving the most satisfactory results.

From the foregoing results it appears reasonably certain that in order to obtain reliable and comparable results the standard and the unknown solution must always contain the same quantities of nitric acid and of molybdate and be at the same temperature.

Should different workers use different amounts of reagent, their results could not be strictly comparable.

EFFECT OF FILTER-PAPER.

In the experiments on the removal of silica and also in some of those on the loss of phosphoric acid on evaporation of the solution, it was observed that the readings were higher than they should have been. As all the work was done in platinum dishes the only point where other material could get in was where the solutions were filtered to remove silica. In order to determine if anything is taken up from the filter, solutions of various strength were passed through 7 cm. S. & S. No. 590 paper with the following results:

Parts per million before filtering.	Parts per million after filtering.	Gain, parts per million.
1	1.16	0.16
1	1.14	0.14
2	2.12	0.12
2	2.17	0.17
5	5.01	0.01
5.5	5.50	0.00

The filters were washed until filtrates had a volume of 50 cc. each. The results indicate that in passing through the filter these nitric acid solutions of phosphates have taken up silica, phosphoric acid or organic matter equal to an average reading of 0.15 part per million in four cases, while in two experiments there is no apparent gain. It seems probable that in these latter cases the amount taken up from the paper, is masked by incomplete removal of the phosphoric acid from the paper, in the volume of wash-water used. Beyond a doubt filtration introduces a plus error, which may only be apparent in very dilute solutions. Results given in this paper have been corrected in accordance with the above data.

REMOVAL OF SILICA.

As it is necessary to remove silica from the solution before reading, it was thought that this might be most expeditiously and certainly accomplished by treatment with hydrofluoric acid. Repeated trials, however, showed that this is not true. While the silica was completely removed finally, it was found that it was necessary to remove all hydrofluoric acid before standardizing, as the smallest quantity of fluorides prevented completely the develop-

ment of the color. As at least three evaporations with nitric acid were required to accomplish the removal of hydrofluoric acid, the standard procedure of evaporation with nitric acid and drying at 100° for two hours was returned to.

The writer's experience confirms the statement of Woodman and Cayvan that a single evaporation removes completely the silica from the solution in those cases where lime and magnesia salts are absent, but where lime and magnesia salts are present in considerable quantities, the amount of silica remaining in solution after one evaporation and filtration is too great to be neglected.

For the study of these points a solution of sodium silicate was prepared which, by gravimetric analysis, gave from first evaporation and filtration, 266 parts per million SiO_2; second evaporation and filtration, 2 parts per million SiO_2; third evaporation and filtration, 0 part per million SiO_2; total, 268 parts per million SiO_2.

The filtrate from the third evaporation contained no silica by the colorimetric method. 250 cc. of this silicate solution were transferred and made up to 1 liter, with the view of obtaining a solution containing about as much dissolved silica as is found in many soil extracts.

By calculation from the above determinations this contained 67 parts SiO_2 per million; first evaporation and filtration removed 63 parts SiO_2 per million; second evaporation and filtration removed 2 parts SiO_2 per million; total recovered, 65 parts SiO_2 per million.

By the colorimetric method the solution contained 65 parts SiO_2 per million.

The filtrate from the first evaporation contained, colorimetrically, less than 0.05 part per million, average of four determinations. The filtrate from the second evaporation contained, colorimetrically, less than 0.1 part per million. The filtrate from the third evaporation contained, colorimetrically, less than 0.1 part per million.

In order to determine the effect of the presence of lime and magnesia salts, a solution containing 25 mg. of calcium nitrate and 25 mg. of magnesia was added to portions of silicate solution and silica determined colorimetrically as well as gravimetrically.

Gravimetrically obtained: First evaporation and filtration re-

moved 63 parts SiO_2 per million; second evaporation and filtration removed 5 parts SiO_2 per million; total, 68.

Colorimetrically obtained: 67 parts SiO_2 per million; calculated, 67 parts SiO_2 per million.

Filtrate from the first evaporation gave, colorimetrically, 1.42 parts SiO_2 per million. Filtrate from the second evaporation gave, colorimetrically, 0.1 part SiO_2 per million. Filtrate from the third evaporation gave, colorimetrically, less than 0.1 part SiO_2 per million.

From these results it appears that in the absence of lime and magnesia salts the silica left in most soil solutions after one evaporation may be neglected, but in the presence of these salts two evaporations are necessary.

THE COLORIMETRIC DETERMINATION OF SILICA.

In their study of the effect of silica on the development of color, Woodman and Cayvan[1] found that while some color was developed instantly, it did not reach the maximum intensity in less than from one and one-half to two and one-half hours, and their results further show that the color due to the formation of the ammonium silico-molybdate is about one-tenth that produced by an equivalent amount of ammonium phosphomolybdate. This reaction apparently was used first by Jolles and Neurath[2] for the determination of silica in waters. For our determination of silica a solution of sodium silicate was prepared and the silica determined gravimetrically. Portions of this solution were compared with the standard phosphate solution under identical conditions as to temperature, nitric acid, molybdate solution, and volume. The data obtained are given in the following table:

TABLE VII.—READINGS OF SiO_2 IN TERMS OF P_2O_5.

Preliminary Series.

Mg SiO_2 in solution read.	Mg. P_2O_5 required to equal color produced by SiO_2.	1 mg. SiO_2 equals mg. P_2O_5.
0.10	0.19	1.90
0.10	0.175	1.75
0.20	0.35	1.75
0.20	0.37	1.85
0.30	0.51	1.70
0.30	0.57	1.90

[1] *Loc. cit.*

[2] *Ztschr. angew. Chem.* (1898), p. 315.

TABLE VII—(*Continued*).

Mg SiO_2 in solution read.	Mg P_2O_5 required to equal color produced by SiO_2.	1 mg. SiO_2 equals mg. P_2O_5.
0.50	0.92	1.84
0.51	0.90	1.78
0.70	1.35	1.93
0.70	1.28	1.83
1.00	1.80	1.80
		Average, 1.82
	Final Series.	
0.068	0.1265	1.86
0.136	0.2464	1.81
0.204	0.3741	1.83
0.272	0.4785	1.78
0.340	0.5907	1.73
		Average, 1.80

The table shows that the intensity of color produced by the silica is on an average 1.8 times that produced by an equivalent amount of phosphoric acid. That is, the phosphate readings divided by 1.8 or multiplied by 0.55 equals SiO_2.[1] It will be seen from the final results, in which most reliance is placed—as they were obtained after considerable experience with the method—that there is a gradual decrease in this factor with increasing quantities of silica. The time required for the full development of the color was much shorter than found by Woodman and Cayvan, apparently reaching the maximum in less than twenty minutes, after which time it remained stationary for some time and then slowly faded.

On the basis of this work the procedure which I have adopted for the determination of silica and phosphoric acid in soil solutions is as follows:

The water or extract is tested for iron by adding potassium ferrocyanide to the acidified solution. The absence of interfering amounts of iron having been shown, a measured volume of the water or soil extract is freed from suspended matter by filtration or by passing through a Chamberland filter (reject the first 100 cc. that passes) or by evaporating to dryness and filtration, or in some cases where the water is but slightly turbid the turbidity or color is corrected for by determining its amount in terms of the

[1] These results differ greatly from those given by Woodman and Cayvan, but so far no time has been available for further study of this point.

standard, the reading thus obtained being afterwards subtracted from the final readings. Add to the clear extract 5 cc. of nitric acid (sp. gr. 1.07) and 4 cc. of molybdate solution. Place in the camera, allow ten to thirty minutes for development of color and compare with a standard phosphate solution, which may conveniently contain 10 parts per million of phosphorus pentoxide and be contained in a sliding tube connected by rubber tubing with a side neck tube graduated in cubic centimeters within the camera. (The color of the standard is not affected by the rubber tube during one working day, but the standard should be made fresh each day.) The readings thus obtained (several should be made and the average taken) minus the reading for turbidity, when calculated to a volume of 100 cc., equals $P_2O_5 + SiO_2$ in parts per million of solution.

Another measured portion of the water or extract is evaporated to dryness twice with a filtration between the evaporations in a porcelain or platinum dish with 3 cc. nitric acid (sp. gr. 1.07) plus a little magnesium nitrate,[1] heated two hours in a water oven, 5 cc. nitric acid (sp. gr. 1.07) added, filtered, washed to about 45 cc., placed in a camera and compared. If colored, the reading is noted, and is finally subtracted from the total reading. Add 4 cc. of ammonium molybdate and thoroughly mix. Place in the camera and compare after two to five minutes. The corrected reading calculated to volume of 100 cc. is P_2O_5 in parts per million of solution. This reading subtracted from the $SiO_2 + P_2O_5$ reading and the difference multiplied by 0.55 gives the silica.

Where the original solution is too much colored with organic matter to be accurately corrected for by reading the color thus produced against the standard phosphate solution, it is necessary to evaporate with about 0.1 gram magnesium nitrate[1] and burn off the organic matter, take up with water + 3 nitric acid, evaporate to dryness and heat two hours in the water oven. Add 5 cc. nitric acid and proceed as above. Readings = P_2O_5. In this case silica is not determined.[2]

The results given in the following table have been obtained in the course of the work.

[1] In solutions containing sufficient base to form normal phosphates with all the phosphoric acid, the addition of magnesium nitrate appears to be unnecessary.

[2] Or the organic matter may be destroyed by treating with aqua regia in the presence of sufficient base to prevent loss of phosphoric acid.

TABLE VIII.—DETERMINATION OF $SiO_2 + P_2O_5$ IN MISCELLANEOUS SAMPLES.

	SiO_2 present.	SiO_2 found.	P_2O_5 present.	P_2O_5 found.
	Parts per million.		Parts per million.	
Sodium phosphate solution, No. 1	....	....	49.6	48.5
" " " " 2	....	....	99.1	101.4
Sodium silicate solution	182.0	180.5	...	....
Soil extract, No. 13	....	24.4	....	2.0
" " " 14	....	23.4	....	2.95
" " " 15	....	21.2	....	2.95
" " " 16	....	19.1	....	2.95
" " 1st foot	....	17.9	....	7.3
" " 2nd "	....	8.2	....	1.0
" " 3rd "	....	7.8	....	3.1
" " 4th "	....	11.9	....	1.4
" No. 2806, sandy truck soil	....	2.0	....	10.0
" " 2795, loam soil	....	38.0	....	8.0
" " 3, clay soil	....	30.0	....	8.0
" " 2804, " "	....	28.0	3 grav.	4.0
Sodium phosphate solution, original solution[1]				73.1
" " " first 50 cc. through Chamberland filter				59.1
" " " second 50 cc. " " "				67.6
" " " third 50 " " "				71.8
" " " left in 50 " in "				80.3
" " " rinsings of "				80.3
" " " original solution				80.25
" " " first 50 cc. through Chamberland filter				54.9
" " " second 50 cc. " " "				71.8
" " " third 50 " " "				84.5
" " " left in 50 " in "				97.2
" " " rinsings of "				84.5

In pure solutions the method gives very close readings and very accurate results on dilute solutions. The average error has been well within 0.2 part per million of the solution read where these solutions did not contain more than 10 parts per million and the readings fall below 60 scale divisions on the colorimeter tube. This insignificant error of reading may give rise to larger differences when calculated on the basis of the dry soil. Should the solution to be examined contain more than 10 parts per million, its dilution to this strength and subsequent calculation to the basis of the original solution or to the dry soil may so multiply this error of reading as to render the results valueless. This has been a serious handicap to the method. The use of more concentrated solutions

[1] Readings made for Professor F. K. King.

is obviously the rational way out of the difficulty. It is also obvious that here we are limited to the use of concentrations from which the phosphomolybdate will not precipitate, within an hour or so. As solutions of greater concentration than 10 parts per million cannot be read closely in 25 mm. tubes, with ordinary light, and as larger tubes were not available, I have not tried greater concentrations in larger tubes, but in several experiments using a strong standard (between 50 and 100 parts per million), in shallow depths in the 25 mm. tubes, it was not found possible to read closer than from 0.5 to 1 part per million. This error of reading, when calculated back to the original solution or to the dry soils, gives as great an error as the closer readings of the more dilute solutions, so this line of study was not carried farther.

In addition to this study conducted with known solutions, the method has also been applied to the soil samples sent out this year by the Association of OfficialAgricultural Chemists. The results thus obtained are given in the following table, with results obtained by the standard methods for determining phosphoric acid. The average total reading in scale divisions and the corrections on each sample, also in scale divisions, are given in the table. These corrections are for original color of the liquid and for filter paper.

TABLE IX.—PHOSPHORIC ACID SOLUBLE IN DISTILLED WATER. PARTS PER MILLION OF DRY SOIL. 400 CC. OF SOLUTION USED FOR THE DETERMINATIONS.

No.	Average total scale readings.	Correction in scale readings.	Reading due to P_2O_5.	P_2O_5, colorimetric.	P_2O_5, volumetric.
2	13.5	1.5	12.0	1.50	1.33
3	10.0	1.5	8.5	1.06	0.64
4	10.0	1.5	7.5	0.94	1.26
5	10.0	3.0	7.0	0.87	0.99
6	48.5	5.5	42.0	5.60	5.10
7	23.0	2.5	20.5	2.56	2.63
8	20.0	3.0	17.0	2.12	1.95

The results given are all that the writer has obtained on soils. No determinations have been rejected.

PRECAUTIONS.

The method is so delicate (one scale division means one-half of one part per million on basis of dry soil when the solution is prepared by treating 1 part of soil with 5 parts of water and taking 50 cc. for the determination), and as has been shown there

are so many points at which errors may be introduced, that a final word as to the precautions to be observed in handling it may be given with propriety.

The sodium phosphate ($Na_2HPO_4 + 12H_2O$) from which the standard is made must be practically pure, and be free from silica and iron. It is convenient to make a solution containing 100 parts phosphorus pentoxide per liter, and then dilute this to 10 parts per liter for the reading standard. The greatest care should be used in making this standard as it is here where errors count. Ten cc. of the 100 parts per liter solution should be run into a standardized 100 cc. flask from an accurately graduated burette. Make up to volume at 20°-25° C. with distilled water (free from $SiO_2 + P_2O_5$), add 10 cc. of nitric acid (1.07) and 8 cc. of ammonium molybdate and mix thoroughly. This is the standard with which the unknown solutions are to be compared and it should be made fresh each day.

All reagents including distilled water must be kept in Jena glassware, tested from time to time and made fresh when a mixture of them shows color after standing some time.

As the colorimetric tubes may have a slight color themselves, each should be tested and its reading carefully established. This may be done by filling the tubes with distilled water and reading them with a 1 part per million standard.

The standard and the unknown solution must contain, in equal volumes, equal amounts of reagents and be at sensibly the same temperature.

The solution must contain less than 20 parts per million of iron (Fe).

A correction must be established for each package of filter-paper used. This correction is small, but not to be neglected on S. & S. No. 590 paper.

When the solution contains much lime or magnesia it is best to make two evaporations and filtrations before comparing.

Observing all precautions and making all corrections there is a maximum error of ± 2 scale divisions (each scale division = 1 cc.) in the reading. When the soil solution is made by treating 1 part of soil with 5 parts of water and 50 cc. are taken for the determination, the error on the dry soil is ± 2 parts per million;

when 100 cc. are taken for the determination the error is ± 1 part per million, so that the working errors may only be neglected when at least 200 cc. of solution are taken for the determination.

BUREAU OF SOILS,
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WASHINGTON, D. C.

A RAPID METHOD FOR DETERMINING SULPHUR IN COAL AND COKE.

BY CARL SUNDSTROM.

Received November 26, 1902.

THE necessity for a rapid method of determining sulphur in fuels, led to the investigation of the action of sodium peroxide on coal. This reaction was suggested by Professor S. W. Parr's paper on his calorimeter as given in this Journal, **22**, 646.

It was found that coal and coke, ignited with a liberal excess of the peroxide, left almost no residue insoluble in a faintly acid solution, and it became a question only of a suitable apparatus. Apparatus was required that would be cheap, in which the charge could be easily ignited, and out of which the melt could be quickly dissolved. For coke, a covered nickel crucible of about 30 cc. capacity answered every purpose; but coal had to be confined in a bomb, as it always burned with explosive violence.

ANALYSIS OF COKE.

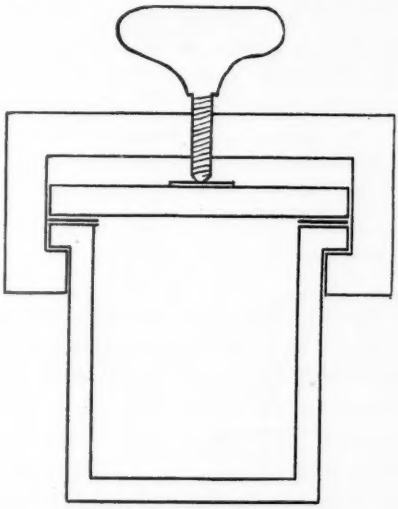
700 milligrams of finely powdered coke are intimately mixed with 13 grams of sodium peroxide, in a nickel crucible of about 30 cc. capacity. The peroxide must be finely powdered and dry, and should be weighed rapidly and brushed off the watch-glass with a glass brush. The crucible is covered and a 3-inch fuse is inserted under the edge of the cover and extended well into the mixture. The crucible is then supported on a triangle and placed in about ¾ inch of water; the fuse is ignited, and in three or four minutes, when the mass has cooled sufficiently, the crucible and cover are placed in a small beaker and 30 cc. water added. The mass dissolves completely in about two minutes. After rinsing off the crucible and cover, the solution is made just acid with hydrochloric acid, and filtered through a small filter. The filtrate is boiled and precipitated with barium chloride in the usual way.

The fuses are made by nitrating cotton wicking with a mixture of 1 part fuming nitric acid (sp. gr. 1.50) and 2 parts concentrated

sulphuric acid (sp. gr. 1.84) for twelve hours, at 15° C. The nitrated cotton is then washed in running water for twelve hours, to remove every trace of acid, and dried at laboratory temperature. When dry, it is treated with a cold, nearly saturated solution of potassium nitrate for an hour; then the excess of solution is pressed out, dried as before, and finally cut into lengths of 3 inches ready for use.

ANALYSIS OF COAL.

The apparatus consists of a small, cylindrical, steel bomb, of the following dimensions: 1¼ inch internal diameter, 1½ inch internal depth, sides and bottom ⅛ inch thick, and a ⅛ inch flange



Sketch of bomb—full size.

around the top. A cover plate $^{3}/_{16}$ inch thick and 1¾ inch in diameter, is clamped on by means of a small clamp, fitting under the bomb flange and pressing down the cover with one central screw. The bottom is hemispherical inside. The cover is insulated from the bomb by a thin mica gasket, and from the screw of the clamp by a piece of ordinary red fiber.

700 milligrams of finely powdered coal are mixed with 13 grams of sodium peroxide in the bomb, and compressed by means of a small press or vice. A No. 36 iron wire, 4 inches long, is now

inserted, one end under the mica gasket and touching the bomb, the other end above the gasket and in contact with the cover, the wire being looped so as to touch the mixture in the bomb. A current of 4 amperes is used to fuse the wire, one terminal in contact with the bomb, the other applied to the cover. After a minute or two, cool the bomb in a little water, unscrew the clamp and dissolve the mass, treating exactly as in the coke analysis.

This method compares very well with Eschka's method and requires much less time and cheaper apparatus while there is less liability of contamination with impure chemicals and exposure to gas flames. The peroxide used seldom contained any sulphates.

The following are some of the results obtained:

Coal and coke.	Per cent. sulphur by Eschka's method.	Per cent. sulphur by peroxide method.
River View coal	1.69	1.64
" " "	1.59	1.57
Hocking Valley, pea	1.95	1.96
" " slack	1.690	1.694
Coke (mixture)	1.26	1.21
Pittsburg coke	0.89	0.88
Connelsville coke	1.67	1.73
Coke mixture	2.027	2.031

DETROIT, October 18, 1902.

A STUDY OF MAGNESIUM AND MANGANOUS HYDROXIDES AND OF BARIUM SULPHATE WITH RESPECT TO THE PHENOMENA OF ADHESION AND OF SOLUTION.

BY HARRISON EASTMAN PATTEN.

Received November 27, 1902.

THE work on aluminum,[1] iron,[2] zinc,[3] and chromium[4] has shown that the action of their hydroxides in carrying down other substances into precipitation is chemical, and under certain conditions not proportional to the mass of precipitate. I have examined the action usually expressed by the equation

$$MgCl_2 + 2KOH = Mg(OH)_2 + 2KCl;$$

also

[1] "A Thermochemical Analysis of the Reaction between Alum and Potassium Hydroxide," *Am. Chem. J.*, **8**, 23.

[2] "A Study of Ferric Hydroxide in Precipitation," *Ibid.*, **19**, 512.

[3] Unpublished.

[4] "Chromic Hydroxide in Precipitation," *Ibid.*, **18**, 608; also "Recherches sur le sulfate chromique, ses transformations et les acides complexes qui en derivent," *Ann. chim. phys.*, **7**, 4 (1895).

$MgCl_2 + 2KOH + K_2SO_4 = Mg(OH)_2 + 2KCl + K_2SO_4$

to ascertain whether magnesium hydroxide acts in a similar manner.

SOLUTIONS.

Solutions as described below were used in the work:

(1) For the magnesium solution, 20.2963 grams of crystallized magnesium chloride was made up to 1 liter at 20°. This solution contained 0.0070 gram chlorine, and 0.00308 gram magnesium oxide per cubic centimeter.

(2) A dilute solution of potassium hydroxide, standardized by oxalic acid and gravimetrically. It contained 0.0261 gram potassium hydroxide per cubic centimeter.

(3) A dilute solution of sulphuric acid, standardized against the potassium hydroxide solution both volumetrically and gravimetrically (weighed as K_2SO_4). It contained 0.04206 gram sulphuric acid per cubic centimeter.

As a preliminary step, the amount of potassium hydroxide required for exact precipitation of the magnesium in Solution (1) was determined.

GENERAL METHOD.

The filtrates were analyzed and the percentage of each constituent found deducted from that of the total introduced. The difference gives the percentage of the constituent in the precipitate, which may not be analyzed directly, since washing or diluting the solution in which the precipitate is formed changes its composition. In the case of magnesium, the precipitated hydroxide is soluble in water.

A blank determination of the magnesium chloride was made: 50 cc. magnesium chloride stock solution was made up to 500 cc. at 20°, four portions were drawn off with a 50 cc. pipette and the magnesium oxide and chlorine determined in duplicate.

$$MgO \begin{cases} 0.0207 \text{ gram} \\ 0.0207 \text{ gram} \end{cases} \qquad Cl \begin{cases} 0.0040 \text{ gram} \\ 0.0042 \text{ gram} \end{cases}$$

Experiments were now made with 44.24 cc. sulphuric acid, neutralized to potassium sulphate by the equivalent amount of potassium hydroxide, and 50 cc. stock solution of magnesium chloride as constant factors, the magnesium being precipitated by varying amounts of potassium hydroxide. The above constituents were

made up to 500 cc. at 20°, allowed to stand twenty minutes, well shaken and four portions of mixed precipitate and solution drawn off with a dry 50 cc. pipette and labeled "totals". The solution and precipitate remaining was thrown upon a dry filter-paper, the clear filtrate brought back to 20°, and five portions drawn off with a 50 cc. pipette and labeled "filtrates".

The "totals" for magnesium oxide were redissolved by hydrochloric acid in some excess, ammonia added to alkaline reaction and the magnesium precipitated cold as magnesium ammonium phosphate, and weighed as pyrophosphate.

The "totals" for chlorine were redissolved by nitric acid, precipitated hot with silver nitrate solution, and the magnesium removed by a wash-water containing 25 cc. concentrated nitric acid and 0.1 gram silver nitrate per liter. The chlorine was then weighed as silver chloride.

The "filtrates" for magnesium oxide and chlorine were analyzed in the same manner as the "totals". As in the work with aluminum, chromium, iron and zinc, it was assumed that re-solution by hydrochloric or nitric acid would liberate any constituents carried down in the precipitation with potassium hydroxide.

It was considered unnecessary to determine the potassium oxide in the "totals" and "filtrates," for two reasons: first, because in all the foregoing work in this line no carrying down of potassium was observed short of re-solution in the alkali; second, the negative results of the work on magnesium oxide, chlorine and sulphur trioxide in this investigation indicate the absence of such action.

No good method of separating the magnesium oxide from the sulphur trioxide in "totals" and "filtrates" being available, two different methods were used to ascertain whether the sulphur trioxide enters into the reaction.

(1) The amount of magnesium oxide precipitated in presence of *potassium sulphate* by a definite amount of potassium hydroxide, should be greater than the amount precipitated in absence of the sulphate—*if sulphur trioxide enters into the reaction.*[1]

(2) Magnesium oxide or chloride should be carried down into precipitation by barium sulphate. The four elements already mentioned show this reciprocal action, as does also manganese, of which I shall speak later.

[1] Series II., "Chromic Hydroxide in Precipitation," *loc. cit.;* "A Study of Ferric Hydroxide in Precipitation," *loc. cit.*

TABLE I.

Experiment.	KOH.	"Total" MgO.	"Filtrate" MgO.	"Precipitate." MgO.	"Total" Cl.	"Filtrate" Cl.	"Precipitate." Cl.	"Precipitate." % MgO.
I	2	0.02065 0.02071 } 0.0207	only a trace	0.0207	0.0036 0.0035 } 0.0036	0.0037 0.0040 } 0.0038	0.0000	100.00
II	6 (2) 300 cc. $MgCl_2$	0.1190+ 0.1190— } 0.1190	0.0026 0.0020 } 0.0023	0.1167	0.2082 0.2085 } 0.2084	0.2086 0.2088 } 0.2087	0.0000	98.06
III	6 (1½) 300 cc. $MgCl_2$	0.1174 0.1180 } 0.1177	0.0281 0.0276 } 0.0278	0.0899	0.2080 0.2085 } 0.2083	0.2081 0.2087 } 0.2084	0.0000	76.38
New solution IV	1½ + K_2SO_4	0.1926 0.1927 } 0.1926	0.0480 0.04807 } 0.0480	0.1446	0.3445 0.3443 } 0.3444	0.3442 0.3438 } 0.3440	0.0004	75.07
V	1½	0.1928 0.1931 } 0.1929	0.0484 0.0481 } 0.0482	0.1447	0.3431 0.3432 } 0.3431	0.3427 0.3429 } 0.3428	0.0003	75.07
VI	1 + K_2SO_4	0.1936 0.1942 } 0.1939	0.0958 0.0963 } 0.0960	0.0979	0.3430 0.3425 } 0.3427	0.3433 0.3429 } 0.3431	0.0000	50.46
VII	1	0.1941 0.1940 } 0.1940	0.0968 0.0966 } 0.0966	0.0974	0.3426 0.3429 } 0.3427	0.3427 0.3426 } 0.3426	0.0001	50.46

Experiment I.—The system was made up according to the equation $MgCl_2 + 2KOH = Mg(OH)_2 + 2KCl$, using 50 cc. of magnesium chloride solution to 22.2 cc. potassium hydroxide solution. No potassium sulphate was introduced here since the object was to determine if chlorine were carried down into precipitation by the magnesium hydroxide. No chlorine was found in the precipitate (see Table I, Exp. I). A trace of magnesium was obtained in the filtrate by further addition of potassium hydroxide, showing that magnesium chloride is not completely precipitated by 2 molecules of potassium hydroxide. As the mass of precipitate was so small, for this concentration, and as "adhesion" in the cases of chromium, iron, aluminum and zinc hydroxides is more marked in concentrated solutions, the next two experiments were made up each with six 50 cc. portions of magnesium chloride solution instead of one 50 cc. portion as in this experiment.

Experiment II.—The system was made up according to the equation $MgCl_2 + 2KOH = Mg(OH)_2 + 2KCl$ (see Table I, Exp. II., for results). This shows no chlorine carried down into precipitation. Since adhesion is more marked at incomplete precipitation than at complete precipitation, in the next experiment I used 1½ KOH.

Experiment III.—The system was made up according to the equation $MgCl_2 + 1\frac{1}{2}KOH = ?$ (see Table I, Exp. III, for results). Here again no chlorine is carried down by the precipitate.

The stock supply of magnesium chloride being now exhausted, a new solution (4) was made up: 203 grams $MgCl_2 + 6H_2O$ were dissolved in water and diluted to 1000 cc. of solution at 20° C. One 50 cc. portion was drawn off and made up to 500 cc. at 20° C. Of this solution each 50 cc. contained:

$$MgO \begin{cases} 0.1926 \text{ gram} \\ 0.1925 \text{ gram} \end{cases} \qquad Cl \begin{cases} 0.3445 \text{ gram} \\ 0.3440 \text{ gram} \end{cases}$$

For 50 cc. of stock solution of magnesium chloride (4), 212.5 cc. potassium hydroxide were required to precipitate completely the magnesium. The calculated amount of potassium hydroxide was 207 cc.

Now the attempt was made to ascertain if sulphur trioxide is carried down into precipitation. As was stated in "General

Method," no good means of separation being at hand a difference method was resorted to. The work on chromium and iron showed that in a partially precipitated system (which had been filtered or allowed to settle) further precipitation was caused by the addition of a little sulphate solution, and in some cases[1] no definite precipitate was obtained unless some soluble sulphate was present. From this influence of sulphur trioxide on the amount of hydroxide formed at fractional precipitation, I assume that if sulphur trioxide is carried down into precipitation by magnesium hydroxide, the amount of magnesium hydroxide precipitated by, say, 1.5 molecules of potassium hydroxide will be greater in the presence of sulphur trioxide than in its absence. If then, the amount of magnesium hydroxide precipitated by 1.5 molecules of potassium hydroxide is the same with and without sulphur trioxide present, I conclude that no adhesion takes place.

For results see Experiments IV, V, VI, VII, Table I, and the accompanying plate, curve 6.

The same amount of magnesia is precipitated in Experiment IV with potassium sulphate present as in Experiment V with potassium sulphate absent; likewise in Experiments VI and VII. Since no sulphur trioxide is carried down into precipitation at these fractional points it was considered unnecessary to try an experiment at complete precipitation, inasmuch as the other elements worked with show their greatest "adhesion" activity at these points. Further, since magnesium gives a definite precipitate at the fractional points in absence of sulphur trioxide, it ought to carry down chlorine into precipitation if it exercises the property of "adhesion"; Experiments I, II, and III show no chlorine carried down.

Experiment VIII.—It was determined that magnesium hydroxide precipitated from magnesium chloride by potassium hydroxide in aqueous solution does not redissolve in excess of potassium hydroxide.

Experiment IX.—Twelve different barium sulphate determinations which had been made from solutions containing magnesium chloride, potassium sulphate and hydrochloric acid by addition of barium chloride were treated as follows: fused with sodium carbonate, the alkali washed out with water, the insoluble barium

[1] Fractional precipitation of chromium chloride by less than three molecules of potassium hydroxide. See "Chromic Hydroxide in Precipitation," *loc. cit.*

carbonate dissolved in hydrochloric acid, reprecipitated by ammonium carbonate to remoe the barium, and the filtrate tested for magnesium by sodium hydrogen phosphate. Not a trace of magnesium was found.

DISCUSSION.

These results may be summarized thus: (1) Magnesium hydroxide does not carry down into precipitation with it either chlorine or sulphur trioxide. (2) Barium sulphate does not carry down into precipitation either magnesium oxide or chloride. (3) More than the theoretical amount of potassium hydroxide is required to completely precipitate magnesium hydroxide from a magnesium chloride solution in water at the concentration and temperature studied. On this last point more work should be done.

MANGANOUS HYDROXIDE.

Method.—The general method used in this investigation was the same as for chromium and iron. The sulphur trioxide was determined directly in "totals" and "filtrates" after the manganese had been removed. This removal was effected in the following manner: Sodium acetate solution was added to the "filtrates" and "totals" and the manganese precipitated as MnO_2 by bromine, the excess of bromine boiled off and the MnO_2 filtered off, well washed, and ignited and weighed as Mn_3O_4. The filtrate from this MnO_2 was concentrated and the SO_3 determined as $BaSO_4$. In the case of the "totals," re-solution of the manganous hydroxide was effected with hydrochloric acid just before the sodium acetate was run in. Occasionally the barium sulphate determinations showed a slight coloration, but the quantity of manganese present was of course negligible. I found this method efficient. Re-solution of these complex precipitates of chromium, iron, manganese, zinc, and aluminum, in hydrochloric or nitric acid has in every case proved sufficient to split them into determinable components.

The chlorine was determined in presence of manganese, a re-solution with nitric acid being first effected, and then all manganese was washed out of the silver chloride by a wash-water containing 25 cc. concentrated nitric acid and 0.1 gram silver nitrate per liter.

Solutions.—*A.* 98.9 grams $MnCl_2 + 4H_2O$ was dissolved in water and made up to 500 cc. at 20° C. This solution was found

to contain the equivalent of 0.05186 gram MnO per cubic centimeter. *B.* A solution of potassium hydroxide containing 0.02705 gram KOH per cubic centimeter at 20° C. *C.* A solution of sulphuric acid containing 0.04046 gram per cubic centimeter at 20° C.

Experiments I, II, III, IV, V were made as shown in Table II. Each system contained 50 cc. manganous chloride, Solution *A*; 44.24 cc. sulphuric acid, Solution *C*, neutralized to potassium sulphate by 75.63 cc. of potassium hydroxide, Solution *B*; and varying amounts of potassium hydroxide to cause the precipitation. In every case the potassium sulphate was run into the flask; next the manganous chloride; and finally the potassium hydroxide. Then the system was made up to 500 cc. at 20° C. and well shaken, whereupon four 50 cc. portions were drawn out with a pipette and labeled "totals." The remaining precipitate and solution were thrown upon a dry filter-paper, the filtrate received in a dry flask, and brought back to 20° C. when four 50 cc. portions were drawn off, and labeled "filtrates." Throughout the investigation of chromium, manganese and magnesium, the same pipette was used.

DISCUSSION.

For results see Table II; also curves 7 and 8 in the plate. The chemical nature of adhesion is clearly shown here as well as in the case of iron, zinc, chromium and aluminum. Experiment I shows no sulphur trioxide in the precipitate, though the mass of precipitate is a maximum. Experiment II shows that 15.34 per cent. of the total sulphur trioxide is in the precipitate, while the mass of precipitate is some 9 per cent. less than in Experiment I. Experiment III shows 19.3 per cent. of the total sulphur trioxide in precipitation, while the mass of precipitate is still less than in Experiment II. Experiment IV confirms Experiment III, giving the maximum sulphur trioxide carried down. Experiment V shows a falling off in the sulphur trioxide in precipitation, but if we remember how small the amount of precipitated manganous hydroxide is at this point (0.5 molecule KOH) the strength of the action is seen to be considerable.

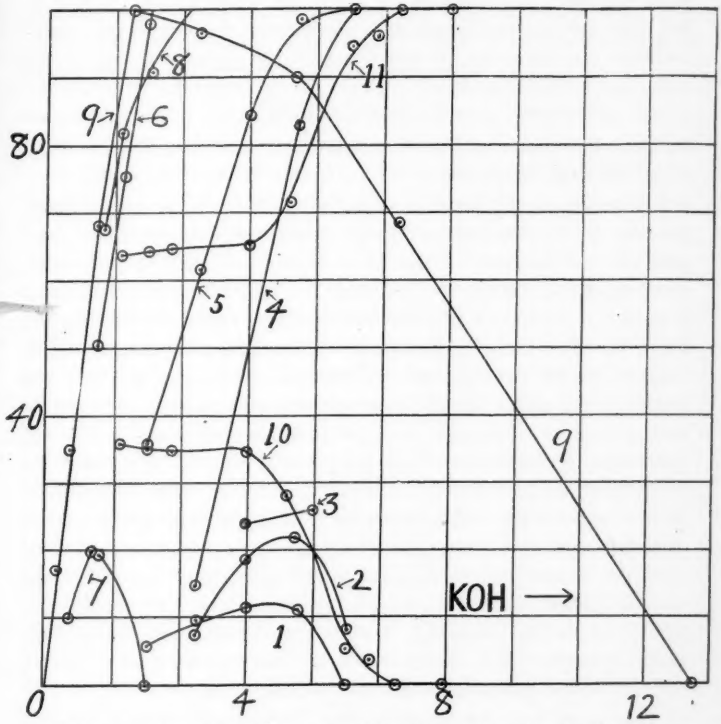
No chlorine was carried down at 1.5 or 1.1 molecules of KOH; hence this "adhesion" is seen to be selective—the sulphur trioxide is taken, and the chlorine left.

TABLE II.

Exp.	KOH + ½K_2SO_4	MnO "total."	MnO "filtrate."	MnO "prec."	SO_3 "total."	SO_3 "filt."		SO_3 "prec."	Cl "total."	Cl "filt."	Cl "prec."	Total % SO_3 in "prec."	Total % MnO in "prec."
I	2	0.2593	0.0146	0.2347	0.1381	0.1379 0.1368		0.0000	.....	.....	.....	....	90.51
II	1½	0.2593	0.04371	0.2122	0.1382	0.1186 0.1154	0.1170	0.0212	0.3307	0.3335 0.3321	0.0000	15.34	81.83
III	$1^1/_{10}$	0.2593	0.0833	0.1760	0.1376	0.1110 0.1111	0.1110	0.0266	0.3298	0.3302 0.3340	0.0000	19.33	67.86
IV	1	0.2593	.....	.....	0 1384	0.1103 0.1106	0.1114	0.0270	.....	.....	.....	19.50	....
V	½	0.2593	.....	.....	0.1378	0.1244 0.1247	0.1245	0.0133	.....	.....	... .	9.65	....

I think it probable that in absence of sulphur trioxide the chlorine would be carried down, since ferric hydroxide shows this same selective action and does carry down chlorine in absence of sulphur trioxide.

Since in the case of iron, potassium appears in the precipitate only at 8 molecules of potassium hydroxide, and in the case of chromium, potassium does not appear at all up to 8 molecules of



potassium hydroxide, it was considered unnecessary to determine potassium in the present investigation.

In the plate, I have plotted curves which show the per cent. of oxide and of sulphur trioxide in the precipitates obtained by adding various amounts of potassium hydroxide to the chloride. Ordinates are in per cent. of constituent; abscissas, in molecules of potassium hydroxide required to produce the precipitate. Curve

1 is the per cent. of total sulphur trioxide in the precipitate of ferric hydroxide; curve 2, the same for chromic hydroxide; curve 3, the same for ferric hydroxide (produced from a solution of ferric chloride having twice the concentration of that used for curve 1).[1] Curve 7 is the same for manganous hydroxide. Curve 4 gives the per cent. of total chromium trioxide precipitated by varying amounts of potassium hydroxide in presence of a fixed amount of potassium sulphate. Curve 5 is the same for ferric oxide. Curve 6, the same for magnesium oxide—presence or absence of potassium sulphate has no effect on the trend of the curve. Curve 8, the same for manganese oxide. Curve 9, the same for zinc oxide.[2] Curve 10 is the per cent. of total sulphur trioxide in the precipitate whose remaining constituent is aluminum trioxide, the per cent. of which is given in curve 11.[3]

My results as plotted in curve 7 show that the action of manganous hydroxide in carrying down sulphur trioxide into precipitation is truly chemical in nature, since the maximum carrying-down effect is observed far short of the maximum quantity of manganous hydroxide, as may be seen by reference to curve 8. The carrying down of chlorine and of potassium oxide remains to be investigated.[4] The results show, too, that the standard equations for the reaction between manganese chloride and potassium hydroxide, and between magnesium chloride and potassium hydroxide in aqueous solution do not represent the facts (see curves 6 and 8; likewise, 9 and 11). The distribution of the constituents of these systems is dependent upon temperature, concentration, and the relative masses of the constituents. Further, the composition of the precipitates as given in the tables and curves considers the precipitate as anhydrous; unquestionably much water is combined in the gelatinous precipitates here studied, but owing to the lack of a method of getting at it quantitatively it has purposely been left unconsidered.

This work has a bearing on the subject of colloidal solution. Reference to a former paper will show that it is possible to form a

[1] Curves 1, 3, and 5 are taken from the thesis of V. J. Hall, *loc. cit.*

[2] C. E. Linebarger: This Journal, **17**, 358 (1895).

[3] Taken from Table VI. A. V. E. Young, *loc. cit.*

[4] This work was done in 1896 and I have kept it back, hoping to make the data more complete; however, circumstances have not permitted of it, and do not at present. These results are of interest to those working on precipitation and solution, so I do not feel justified in withholding them longer.

colloidal solution containing chromium chloride, potassium chloride and potassium hydroxide all combined with each other and with water so that the equation,

$$2CrCl_3 + 3KOH = CrCl_3 + Cr(OH)_3 + 3KCl,$$

does not represent the true state of the system. If any soluble sulphate be added, this colloidal solution gelatinizes. A nitrate or chloride will not produce this effect. It seems to me that this reaction disposes of the idea which had been advanced that *any electrolyte* will precipitate a colloid.[1] Here certainly the colloid seems to have a decided preference for sulphates.

BARIUM SULPHATE.

To examine further this "adhesion" phenomenon, samples of barium sulphate were prepared in two ways: (1) Precipitated with sulphuric acid from barium chloride dissolved in water, and the washed barium sulphate boiled for several hours with the aqueous solution of some metallic chloride. (2) Precipitated with sulphuric acid from an aqueous solution of barium chloride containing the same metallic chloride used in Method (1).

These samples enable one to decide whether the coloration of barium sulphate which is observed in samples precipitated in presence of salts of iron, manganese, chromium, etc., is necessarily enclosed when the crystal forms.

In this way I prepared samples of barium sulphate containing nickel, cobalt, manganese, chromium, iron and copper, and examined them under a high-power microscope. The crystals were measured by a stage and eye-piece combination micrometer, and averaged 0.00005 to 0.000125 inch in diameter.

No difference in shade could be detected between barium sulphate crystals prepared by Method (1) and those obtained by Method (2) with any of the metals used. The coloration was well marked and was compared with that of freshly prepared pure barium sulphate on the same glass side.

These results indicate that the metals given can penetrate barium sulphate crystals after they are formed and find lodgment there. But once these metals are in the barium sulphate crystal it is, as every analyst knows, no easy matter to get them out. From this we might, without doing violence, argue for chemical combination between the barium sulphate and the metal (or its salt or oxide). Further, chromic chloride in aqueous solution is

[1] "Chromic Hydroxide in Precipitation," *loc. cit.*

known to dissolve barium sulphate crystals in appreciable amount. This shows that we have here a case of mutual action, the barium sulphate dissolving the chromium (in some form) and the chromium chloride in water dissolving the barium sulphate. As the barium sulphate remains solid, we have another case of a solid solution and a liquid solution coming into equilibrium in such a way as to give ground for believing that solid solution and liquid solution are of the same order, and to be classed as chemical combinations of solvent with solute.

I wish to thank Professor A. V. E. Young, of Northwestern University, for many helpful suggestions given me during the progress of this work.

CHEMICAL LABORATORY, UNIVERSITY OF WISCONSIN,
MADISON, November 26, 1902.

[CONTRIBUTION FROM THE HAVEMEYER LABORATORIES, COLUMBIA UNIVERSITY, No. 65.]

THE GRAVIMETRIC DETERMINATION OF MERCURY AND ITS SEPARATION FROM ARSENIC, ANTIMONY, AND COPPER.

BY CHARLES J. PRETZFELD.

Received December 8, 1902.

HISTORICAL.

Mercury Weighed as Chloride.—For the determination of mercury in this form, the following reducing agents have been proposed: formic acid,[1] ferrous sulphate,[2] phosphorous acid,[3] glucose,[4] potassium hypophosphite,[5] a mixture of hypophosphorous acid and peroxide of hydrogen,[6] and hydrazine sulphate.[7]

Mercury Weighed as Oxide.—The determination of mercury in this form is unimportant, the only method known being that of Marignac.[8]

Mercury Weighed as Metal.—Under this heading, the history of mercury determination can be subdivided into three classes:

(*A*) By application of reducing agents in the cold.

[1] Bonsdorff: *Ann. Chem. Phys.*, **33**, 78.
[2] Hempel: *Ann. Chem. Pharm.*, **110**, 176.
[3] Rose: *Jsb. d. Chem.*, **13**, 665.
[4] Hager: *Ztschr. anal. Chem.*, **17**, 380.
[5] Thompson · *J. Soc. Chem. Ind.*, **16**, 263.
[6] Vanino and Treubert: *Ber. d. chem. Ges.*, **30**, 2808-2809.
[7] Jannasch and Durselen: Doctor's Dissertation at Heidelberg, 1899.
[8] *Jsb. d. Chem.*, (1849), p. 594.

(*B*) By application of heat to volatilize the mercury.

(*C*) By electrolytic deposition.

Under class *A* we have the methods of Mitscherlich,[1] Sieveking,[2] Jannasch and Alffers,[3] and of Jannasch and Durselen.[4]

Under class *B* the methods of Milton,[5] Rose,[6] Eschka,[7] Attwood,[8] Schuyten,[9] Chism,[10] and of Janda[11] are the most important.

Under class *C* the most important methods are those of Hannay,[12] Clarke,[13] Ludwig and Classen,[14] Brand,[15] Vortman,[16] Rudorff,[17] Smith and Moyer,[18] Smith and Wallace,[19] Smith and Kollock,[20] Perreau,[21] and of Classen.[22]

EXPERIMENTAL.

About 8 liters of a solution of mercuric nitrate were made, and used for testing the accuracy of various methods for the determination of mercury. The strength of the solution was found to be, by electrolysis, such that each cubic centimeter contained 0.01673 gram of mercury.

Estimation of Mercury as Sulphide.—The form in which mercury is most commonly weighed being the sulphide, a few experiments were conducted to find how reliable this method is.

Twenty-five cc. of the solution of mercuric nitrate were taken and the mercury precipitated, and purified according to the method of Polstorff and Bulow. The solution was diluted to a volume of 250 cc. and saturated with sulphuretted hydrogen. The precipitate was washed with water containing sulphuretted

[1] *Pogg: Ann. Phys. Chem.*, **9**, 39.
[2] *American Chemist*, **6**, 160.
[3] *Ber. d. chem. Ges.*, Part II, pp. 2381-2385.
[4] Doctor's Dissertation at Heidelberg, 1899.
[5] *Erd. J.*, **37**, 271.
[6] *Erd. J.*, **34**, 36.
[7] *J. Chem. Soc.* (London), (1872), p. 25.
[8] *Chem. News*, **39**, 111.
[9] *J. Soc. Chem. Ind.*, **15**, 475.
[10] *Trans. A. I. M. E.*, **28**, 448.
[11] *J. Soc. Chem. Ind.*, **18**, 610.
[12] *Am. Chem. J.*, **4**, 193.
[13] *Chem. News*, **38**, 273.
[14] *J. Chem. Soc.* (London), **1**, 493.
[15] *J. Soc. Chem. Ind.*, **8**, 1011.
[16] *Jsb. d. Chem.*, p. 2403.
[17] *Ztschr. angew. Chem.*, (1892), p. 5.
[18] *Ztschr. anorg. Chem.*, **4**, 96.
[19] This Journal, **18**, 169.
[20] Doctor's Dissertation, at Univ. of Penna., 1899.
[21] *J. Soc. Chem. Ind.*, **19**, 53.
[22] "Ausgewählte Methoden der Analytischen Chemie," Ed. 1901, p. 49.

hydrogen, and was then dissolved in a solution prepared by mixing a 15 per cent. solution of potassium sulphide with an equal volume of a 15 per cent. solution of caustic potash. The solution thus obtained was heated to 80° C. and upon addition of ammonium chloride, the mercury was reprecipitated as sulphide. This precipitate was washed with a solution of sulphuretted hydrogen, then twice with water, once with alcohol, twice with carbon bisulphide, and again with alcohol, dried at 100° and weighed.

RESULTS.

$Hg(NO_3)_2$ solution. Cc.	Calculated to Hg. Gram.	Weight of HgS found. Gram.	Calculated to Hg. Gram.
25	0.41825	0.4919	0.4239
19	0.31787	0.3734	0.3216
10	0.1673	0.1665	0.1693

Estimation of Mercury as Chloride.—The first method tried was that of Hempel, and was carried out as follows:

A known quantity of the standard solution of mercury was diluted to 150 cc.; 0.3 gram sodium chloride and 1.8 grams ferrous sulphate were then added and the solution stirred until the salts added had dissolved. Caustic soda was next added until the solution had become alkaline, and the whole was stirred for a few minutes. Sulphuric acid was then added to acid reaction and the solution again stirred. The solution was then allowed to stand over night. The precipitate was filtered off and washed once or twice with cold water, dried at 100° C., and weighed.

RESULTS.

$Hg(NO_3)_2$ taken. Cc.	Calculated to Hg. Gram.	Weight of Hg_2Cl_2. Gram.	Calculated to Hg. Gram.
(*A*) 25	0.41825	0.4898	0.4161
(*B*) 25	0.41825	0.4896	0.4159
(*C*) 25	0.41825	0.4906	0.4167
(*D*) 25	0.41825	0.4905	0.4166
(*E*) 17	0.2844	0.3355	0.2849
(*F*) 15	0.2509	0.2926	0.2490

The next method tried was that of Vanino and Treubert, in which an excess of sodium chloride is added to the solution of mercury, which should have a volume of about 100 cc., and then as a reducing agent a slight excess of a mixture containing one drop of commercial hypophosphorous acid to every cubic centimeter of peroxide of hydrogen is added drop by drop, while stirring. The solution is allowed to stand one hour, filtered on balanced filters

and quickly washed with hydrochloric acid, and finally with water. The temperature used for drying was 105° C.

RESULTS.

$Hg(NO_3)_2$ taken. Cc.	Calculated to Hg. Gram.	Weight of Hg_2Cl_2. Gram.	Calculated to Hg. Gram.
25	0.41825	0.4893	0.4156
25	0.41825	0.4892	0.4155
21	0.35133	0.4105	0.3486
10	0.16730	0.1955	0.1660
15	0.25096	0.2937	0.2494

By a slight modification of this method, very accurate results were obtained. Instead of converting the mercury and then reducing, the reducing agent was added first and after stirring for about one minute, an excess of sodium chloride was added. A heavy curdy precipitate, very similar in appearance to that of silver chloride, was thrown down immediately and settled very rapidly. The other conditions of the above method were maintained. The accuracy of the results obtained in this manner can be judged from the following table.

RESULTS.

$Hg(NO_3)_2$ taken. Cc.	Calculated to Hg. Gram.	Weight of Hg_2Cl_2. Gram.	Calculated to Hg. Gram.
13	0.21749	0.2556	0.2171
19	0.31787	0.3736	0.3173
15	0.25095	0.2951	0.2506
15	0.25095	0.2953	0.2508
10	0.16730	0.1972	0.1675
10	0.16730	0.1972	0.1675
10	0.16730	0.1971	0.1674

The explanation for the rapid formation of this precipitate, is that mercury in the form of nitrate is reduced, and this salt of mercury being much more dissociated than the chloride, the reaction takes place in a much shorter period of time. The disadvantage of the above is, however, that mercury is usually in the form of chloride, and for this reason the method cannot be applied very generally.

The next method tried was that of H. Rose. It was conducted in exactly the same manner as that of Vanino and Treubert, the only difference being that phosphorous acid is used as a reducing agent, and that the precipitate was allowed to settle over night. The results are quite low, probably due to the strong reducing action of phosphorous acid. The precipitate had a grayish color

and also showed a tendency to run through the paper. The results obtained are as follows:

RESULTS.

$Hg(NO_3)_2$ taken. Cc.	Calculated to Hg. Gram.	Weight of Hg_2Cl_2. Gram.	Calculated to Hg. Gram.
25	0.4182	0.4881	0.4146
14	0.2342	0.2726	0.2316
17	0.2844	0.3311	0.2812
13	0.2175	0.2530	0.2149
17	0.2844	0.3313	0.2814
20	0.3346	0.3913	0.3324

When the reducing agent was added before converting the mercury to chloride, the following results were obtained:

RESULTS.

$Hg(NO_3)_2$ taken Cc.	Calculated to Hg. Gram.	Weight of Hg_2Cl_2. Gram.	Calculated to Hg. Gram.
10	0.1673	0.1970	0.1673
15	0.2509	0.2959	0.2514
10	0.1673	0.1968	0.1671
10	0.1673	0.1963	0.1667

The quality of the precipitate obtained in this way was the same as that obtained by similarly modifying Vanino and Treubert's method.

Estimation of Mercury as Arsenate.—Since the percentage of mercury in mercury arsenate is smaller than in mercury sulphide or chloride, the error caused by manipulation will of course be smaller than if the mercury formed a larger proportion of the precipitate. That an arsenate of mercury exists, is known,[1] but no attempt had ever been made to weigh the mercury in this form. Those conditions were consequently sought which would precipitate the metal completely and give the most accurate results. By the following method good results were obtained. To a cold solution of mercuric nitrate, of a bulk of about 100 cc., about 20 cc. of a saturated solution of sodium arsenate was added, this being an excess. A heavy yellowish-white precipitate of mercuric arsenate was immediately formed, and settled rapidly, but in order to insure complete precipitation, it was found best to allow the solution containing the precipitate to stand for about five hours. The solution was then filtered through balanced papers, and the precipitate was washed with cold water, dried at 95° C. to 100° C. and weighed.

[1] Damner's "Anorganische Chemie," II, p. 921.

RESULTS.

$Hg(NO_3)_2$ taken. Cc.	Calculated to Hg. Gram.	Weight of $Hg_3(AsO_4)_2$ Gram.	Precipitate calculated to Hg. Gram.
15	0.2509	0.3674	0.2509
15	0.2509	0.3677	0.2512
15	0.2509	0.3671	0.2508

These results are sufficiently accurate for any requirements, and the method is extremely simple. Unfortunately, however, the mercury is not precipitated as arsenate from a chloride solution, thus limiting the application of the method considerably. The presence of a small amount of free nitric acid did in no way interfere with the accuracy of the results.

Electrolytic Determination of Mercury.—Two methods only were used, the purpose having been more to determine the strength of the standard solution used, than to compare the methods.

In the first method the conditions proposed by E. F. Smith were tried.

RESULTS.

$Hg(NO_3)_2$ Cc.	KCN. Gram.	Dilution. Cc.	Current.	Voltage.	Temperature. °C.	Mercury found. Gram.
10	0.8	100	$N.D._{100} = 0.07$ A	3.2	65	0.1675
10	0.8	100	$N.D._{100} = 0.07$ A	3.2	65	0.1663

The other method was from a solution of the double sulphide of mercury and potassium. The conditions and results were:

$Hg(NO_3)_2$ Cc.	K_2S. Cc.	Dilution. Cc.	Current.	Voltage.	Temperature. °C.	Mercury found. Gram.
10	20–25	125–130	$N.D._{100} = 0.12$ A	2½	70	0.1672
10	20–25	125–130	$N.D._{100} = 0.12$ A	2½	70	0.1673

From these results, the strength of the solution in terms of mercury was 0.01673 gram for each cubic centimeter.

All of the most important methods for the gravimetric estimation of mercury having been tried, it was concluded that, when accuracy is desired, the following methods, only, will give satisfactory results.

First, the method of Vanino and Treubert, as modified, page 201.

Second, the method of Rose, as modified, page 201.

Third, the determination of mercury as arsenate, described on page 202.

Fourth, the determination of mercury by electrolysis.

Unfortunately the first, second and third methods above re-

ferred to cannot be used when the mercury is in the form of chloride, the first and second yielding low results, and the third being impossible since no precipitate is formed. The precipitation of mercury as sulphide, on the other hand, permits of very wide application. The precipitation as such is always rapid as well as complete, but if weighed in this form it yields high results on account of the separated sulphur present. The precipitation in this form is however of great value, not only because it acts in many cases as a separation, but also because the precipitate can easily be dissolved and electrolyzed from the solution thus obtained, yielding most satisfactory results. This method was used in the succeeding work on the separation of mercury.

The Separation of Mercury from Arsenic, Antimony and Copper.—The most important methods for this separation are those of Rose,[1] Fresenius,[2] Polstorff and Bülow,[3] v. Uslar,[4] Jannasch and Lenhert,[5] Jannasch and Devin,[6] and Jannasch and Durselen.[7]

As these methods either afford low results or require an excessive amount of manipulation, a simpler and more accurate method was sought.

EXPERIMENTAL.

Separation of Mercury from Antimony and Copper by the Use of Sulphuretted Hydrogen in a Cyanide Solution.

Separation of Mercury from Copper.—Although it was already known that mercury could be separated from copper by saturating a cyanide solution of the two metals with sulphuretted hydrogen,[8] no attempt has been made to separate mercury from antimony and arsenic by a method based on the same, or on a similar principle. Before going further, it was considered advisable to test the accuracy of the method of Haidlen and Fresenius for the separation of mercury from copper. The results were found to be satisfactory.

[1] *Jsb. d. Chem.*, **13**, 665.
[2] *Ztschr. anal. Chem.*, **2**, 343 (1863).
[3] *Ibid.*, **31**, 697.
[4] *Ibid.*, **34**, 411.
[5] *Ztschr. anorg. Chem.*, **12**, [5]. 359-364.
[6] *Ber. d. chem. Ges.*, **31**, 2, 2377-2385.
[7] Doctor's Dissertation, Heidelberg, 1899 ; *Ibid.*, Heidelberg, 1899.
[8] Haidlen and Fresenius : *Ann. Chem. Pharm.*, **43**, 144 (1842).

RESULTS.

$Hg(NO_3)_2$ taken. Cc.	$Hg(NO_3)_2$ calculated to Hg. Gram.	Cu taken. Gram.	Hg found. Gram.
9	0.1505	0.05	0.1497
10	0.1673	0.05	0.1666
10	0.1673	0.05	0.1670
10	0.1673	0.05	0.1667
10	0.1673	0.15	0.1672
10	0.1673	0.15	0.1674
10	0.1673	0.30	0.1671
10	0.1673	0.30	0.1670

Separation of Mercury from Antimony and Copper.—The above method was tried for the separation of mercury from solutions containing antimony and copper, and although good results were obtained, the process was inconvenient owing to the partial precipitation of antimony, upon adding potassium cyanide. In the presence of tartaric acid, it was found that antimony remains completely in solution and that upon saturating the solution with sulphuretted hydrogen, only mercury is precipitated.

Separation of Mercury from Antimony, Arsenic and Copper by the Use of Tartaric Acid, Potassium Cyanide and Sulphuretted Hydrogen.

Separation of Mercury from Antimony and Copper.—To a clear solution of the three metals, about 30 cc. of a saturated solution of tartaric acid was added and the solution stirred for one or two minutes. Potassium cyanide was then added in small amounts at a time, until the solution became clear. While adding the latter reagent, it was found necessary to stir the solution continually in order to dissolve the potassium cyanide. Hydrogen sulphide was then led into the solution, until saturated, and the precipitate of mercury sulphide was allowed to settle. This precipitation was performed in the cold, as there is some danger of losing a little mercury with the escaping fumes. The precipitate of mercury sulphide was then filtered, dissolved and electrolyzed.

RESULTS.

$Hg(NO_3)_2$ taken. Cc.	Calculated to Hg. Gram.	Sb taken. Gram.	Cu taken. Gram.	Hg found. Gram.
10	0.1673	0.10	0.10	0.1672
10	0.1673	0.10	0.10	0.1665
8	0.1338	0.20	0.20	0.1328
9	0.1505	0.20	0.20	0.1509
11	0.1840	0.30	0.30	0.1840
12	0.2007	0.30	0.30	0.2005
9	0.1505	0.10	0.30	0.1510
10	0.1673	0.10	0.30	0.1669
8	0.1338	0.30	0.10	0.1339
11	0.1840	0.30	0.10	0.1844

The conditions for this separation were found to be very broad, thus rendering the method one which can be carried out with great facility. The minimum amount of potassium cyanide required is an excess of 1 or 2 grams. It is safer to add an excess of 2 or 3 grams so that the solution will be strongly alkaline. Any excess beyond this amount does no harm. The dilution also permits of wide limits. The smallest bulk which was used in the above determinations was about 150 cc. and the largest about 500 cc. In both of these experiments the results were accurate. Furthermore, the solution, alkaline with potassium cyanide, was allowed to stand for more than two hours, with no perceptible change. Nor did standing for two or three hours after precipitation with hydrogen sulphide interfere in any way with the final result. The advantage of the tartaric acid in the solution, over the method first attempted, where no tartaric acid was used, is firstly, that no precipitate of antimony is formed, thereby avoiding the necessity of an additional filtration, and in case a determination of antimony is required, the solution of this precipitate is avoided. The red color formed in the former method is completely absent in the presence of this acid. In most, if not all cases, however, the solution becomes pale orange, which is not in the least an objection. Again when no tartaric acid is used, it is always fatal to use potassium cyanide, containing sulphur[1] since mercury is precipitated as sulphide and is consequently filtered off with the antimony and copper. When, on the other hand, tartaric acid is present, a black precipitate of mercury sulphide is formed which can be filtered off with the main precipitate of mercury sulphide, precipitated by hydrogen sulphide.

Separation of Mercury from Arsenic, Antimony and Copper.— The next separation attempted under these same conditions was the separation of mercury from arsenic. A solution of sodium arsenate was made up of a strength of about 1 per cent. of metal. The results of the separations were very satisfactory.

RESULTS.

$Hg(NO_3)_2$ taken. Cc.	Calculated to Hg. Gram.	As taken Gram.	Hg found. Gram.
8	0.1338	0.05	0.1342
10	0.1673	0.05	0.1670
11	0.1840	0.30	0.1833
9	0.1506	0.30	0.1511

[1] Potassium cyanide free from sulphur is a very expensive reagent.

To determine if mercury could be separated from antimony, arsenic and copper, experiments were made with the following results:

$Hg(NO_3)_2$ taken. Cc.	Calculated to Hg. Gram.	Cu taken. Gram.	Sb taken. Gram.	As taken. Gram.	Hg found. Gram.
9	0.1506	0.05	0.05	0.05	0.1509
9	0.1506	0.05	0.05	0.05	0.1507

It was also attempted to separate mercury from tin but the results were very low. This, although it could not be accounted for, is of interest, since, in the method of Polstorff and Bülow where mercury is separated by dissolving the sulphide in alkaline sulphide and then reprecipitating it as sulphide on addition of ammonium chloride, some mercury is also withheld by tin if present.[1] The method of v. Uslar,[2] in which phosphorous acid is used to separate mercury from the metals of the fifth and sixth group is useless also, if tin is present. Bismuth and lead, if present, are completely precipitated with the mercury as sulphides, from which they are separated by digestion with an alkaline sulphide.

MERCURIAL ORES.

A. Analysis of Cinnabar.—Cinnabar, being the most important ore of mercury, it seemed well worth while to compare one or two of the most important methods for the determination of that metal therein.

The most important methods for the determination of mercury in cinnabar are those of Classen,[3] Rising and Lenher,[4] Smith and Wallace,[5] Chism[6] and a number of distillation methods.

By the method of Smith and Wallace, the ore was found to contain 16.0 per cent. and 16.02 per cent. of mercury. Chism's method was tried with various modifications, yielding the following results:

Ore taken. Gram.	Hg found. Per cent.
0.29755	13.81
0.22440	13.68
0.1661	15.35
0.1301	15.14
0.1384	15.32
0.1384	13.87
0.4625	13.91

[1] Classen: "Ausgewählte Methoden der Analytischen Chemie," p. 63.
[2] *Ztschr. anal. Chem.*, **34**, 391 (1895).
[3] "Ausgewählte Methoden der Analytischen Chemie," Ed. 1901, p. 50.
[4] This Journal, **18**, 96 (1896).
[5] *Ibid.*, **18**, 169 (1896).
[6] *Trans. A. I. M. E.*, **28**, 148 (1898).

Another method tried on cinnabar was the distillation of a large amount of mercury from the ore, which had been mixed with iron filings. An ordinary glass retort was used and the mercury was caught in very dilute hydrochloric acid. The purification of the mercury was carried out by treatment with successive portions of dilute hydrochloric acid. It was finally poured into a weighed porcelain crucible and dried after having been washed with alcohol, two or three times.

RESULTS.

Ore taken. Grams.	Iron filings taken. Grams.	Hg found. Grams.	Hg found. Per cent.
22.5214	175	3.5163	15.61
24.1709	180	3.7402	15.47

B. Analysis of Mercurial Tetrahedrite.—Although earnest and repeated efforts were made to procure specimens of mercurial tetrahedrite, the only one that could be obtained contained but 0.3 per cent. of mercury. This was considered too low to show a just comparison of the methods, so a mixture of cinnabar and tetrahedrite was made and analyzed in the same way.

In applying the method in which tartaric acid and potassium cyanide are used, the decomposition of the mineral and mixture were effected in the manner described by Rose and Wöhler. The solution obtained was then filtered. To the filtrate, tartaric acid was added, then potassium cyanide and this was followed by the addition of sulphuretted hydrogen. The precipitate of mercuric sulphide was then filtered from the solution and treated as already described. If lead and bismuth are present, they also will be precipitated and can be separated from the mercuric sulphide by any of the well-known methods. All of the other metals likely to be found in tetrahedrite remain in solution.

RESULTS.

Amount of mineral taken. Gram.	Mercury found. Gram.	Mercury. Per cent.	
0.9153	0.0012	0.13	Method of Rose and Wöhler.
1.0474	0.0014	0.13	
1.0500	0.0015	0.14	
1.1986	0.0042	0.35	Tartaric acid and potassium cyanide method.
1.0278	0.0039	0.38	
0.8581	0.0756	8.81	Method of Rose and Wöhler.
0.8989	0.0805	8.95	
1.0310	0.0931	9.03	
0.8853	0.0845	9.54	Tartaric acid and potassium cyanide method.
0.9139	0.0874	9.56	
0.8592	0.0814	9.47	

These results show conclusively that the separation of mercury from arsenic, antimony, and copper, by the use of tartaric acid and potassium cyanide is more complete and consequently more accurate than by the use of ammonium sulphide.

Chism's method also was tried on the tetrahedrite, with good results. This seems to prove this method very good for ores running low in mercury.

The results obtained by Chism's method were 0.27 per cent. and 0.33 per cent. of mercury.

As this work was carried out under the suggestion and guidance of Professor E. H. Miller, it is but just and proper, that any merit which it may possess be associated with his name.

QUANTITATIVE LABORATORY,
May, 1902.

NOTE CONCERNING THE CALCULATION OF THERMOCHEMICAL RESULTS.

BY THEODORE WILLIAM RICHARDS.

Received December 10, 1902.

IT is well known that the heat capacities of the majority of reacting substances change during their reaction. The magnitude of these changes and their significance are nevertheless often neglected.

A serious error may arise from this neglect. For example, according to the results of Thomsen, the neutralization of an approximately half normal solution of sodium hydroxide by an equivalent solution of hydrochloric acid involves an increase of heat capacity of 1.27 per cent.[1] The question now arises, since the solutions themselves are the capacities being warmed, What value for the total heat capacity shall be used in the calculation of the heat of reaction? Obviously the energy-change will be found to be 1.27 per cent. greater if the final, rather than the initial, heat capacity is used. The answer to this question is variously given in the different authorities upon thermochemistry. Ostwald and Luther in their admirable handbook[2] use the sum of the initial heat capacities; Thomsen often uses the capacity of the water alone; Berthelot commonly considers the capacity as equal to that

[1] Thomsen: "Thermochemische Untersuchungen," I, p. 67 (1882).
[2] Ostwald-Luther: *Physiko-Chemische Messungen*, (1902), p. 214.

of the same volume of water, and Wiedemann and Ebert,[1] as well as Traube,[2] recommend similar crude approximations.

It is probable that all of these writers understood wholly the conditions involved by their respective methods, but it is certain that they have not made this understanding clear to the public. The resulting frequently observed confusion among students of physical chemistry concerning this point has therefore led to the present paper. This paper does not pretend to claim originality; it is designed rather to further a general comprehension of the subject, and thus to add to precision of work and statement.

Obviously, since changing heat capacity means changing heat of reaction with changing temperature,[3] the precise thermochemical reaction should be conducted isothermally. In many cases, Waterman's method, which consists in dropping into a warming mixture known weights of cold material and vice versa,[4] may make this isothermal performance possible. Here the calculation is very simple, for the heat capacity to be considered is merely that of the compensating foreign material,—unless indeed this substance in the act of mixing changes its own heat capacity. Waterman's method is, however, rarely employed; the more usual method is to allow the reacting substances to raise or lower the temperature of their resulting mixture adiabatically, that is, without releasing or gaining heat. Nothing could be simpler than the calculation of this adiabatic process in terms of an isothermal one; and this calculation at once clears away the confusion before mentioned.

Imagine for the sake of definiteness a warming reaction. According to the first law of energy, the isothermal evolution of heat in the reaction may be as well measured in two stages as in one. Hence, after the reaction is completed without loss of heat, the mixture may be cooled down to the original temperature; and the heat given out during this cooling will be the total heat of reaction at that temperature. This value will be found by multiplying the heat capacity of the *product* of the reaction by the change of temperature, since it is this product which is to be cooled.

The proceeding may be represented graphically by the right-

[1] Wiedemann-Ebert: *Physikalisches Praktikum* (1899).

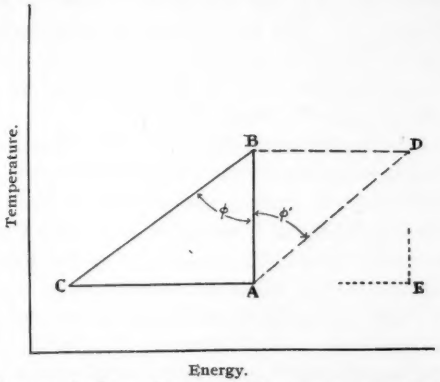
[2] Traube's (trans. Hardin): "Physical Chemical Methods," 1898.

[3] Kirchhoff's Law; see also Thomsen: "Thermochemische Untersuchungen," I, p. 65 (1882).

[4] Waterman: *Phys. Rev.*, **4**, 161 (1896); see also Cady: *Jour Phys. Chem.*, **2**, 561 (1898).

angled triangle A B C in the accompanying diagram, in which A represents the initial state of the system, A B the adiabatic process, B C the cooling process, and A C the desired isothermal loss of energy.

Does this demonstration, proving that the capacity of the *products* must be used in order to obtain the true heat of reaction at the initial temperature, render valueless a knowledge of the capacity of the factors? Not at all; for it is easy to show that the heat of reaction computed from the specific heats of the *factors* is that corresponding to the *final* temperature. Let us consider the



same reaction as before, between the same temperatures. The adiabatic effect will be precisely the same as before. But in order that the heat capacities of the factors may be used, and the total process still be isothermal, it is obvious that the factors must first be cooled from a temperature which is to be the final one, to that from which the adiabatic reaction is to start. This cooling, represented above by the line D A, is immediately followed by the adiabatic reaction A B, which brings the system to the same temperature as D. During this double process, the system at the final temperature has lost an amount of energy represented by D B, all of which was removed by the cooling of the factors.

In brief, *the total heat capacity of the product must be multiplied by the change in temperature in order to compute the heat of reaction at the initial temperature, while the total heat capacity of the factors must be so multiplied in order to compute the heat of reaction at the final temperature.* This statement applies to a cooling reaction as well as to a warming reaction. If, as is often

the case, the total energy change at an average temperature is desired, the average of the two total heat capacities must be used in the computation. If the two factors have at first different temperatures, their effects must be computed separately and the resulting heat of reaction must be referred to the final temperature. When there is an accidental outside warming or cooling effect, the corrected temperatures should be used.

A slight inexactness lies in the italicized statement, due to the fact that specific heat itself is variable with temperature. Therefore, the heat capacities of the initial and final systems are not in reality perfectly constant, and the lines B C and D A should not be perfectly straight. This deviation is nevertheless usually very slight in dilute aqueous solutions; and until the whole body of physicochemical data attains a much greater degree of accuracy than at present, it may be neglected.

Evidently the quadrilateral figure C A B D may be used to demonstrate trigonometrically the rule of Kirchhoff—the familiar relation which lies at the basis of the question treated in this paper. The reaction may proceed from A to B by two simple indirect paths. According to one, the reaction may be allowed to take place isothermally, at the lower temperature, involving the loss of energy, A C, and the products may then be warmed to a higher temperature involving a gain of energy, C B, while according to the other the factors may be warmed to the higher temperature, A D, and the reaction there allowed to proceed isothermally to B by the loss of energy, D B. In this demonstration it is of course unnecessary to place B exactly over A, a condition which ensues only when the higher temperature is that actually attained by the adiabatic reaction. Obviously, from inspection of the diagram,

$$CE = CA + AB \tan \phi' = BD + AB \tan \phi;$$

$$CA - BD = AB (\tan \phi - \tan \phi').$$

Now $(CA - BD) = U_T - U_{T+t}$, the difference between the heats of reaction at the two temperatures; $\tan \phi$ or $\frac{CA}{AB}$ represents the heat capacity of the products (K_2); $\tan \phi$ or $\frac{BD}{AB}$ represents the heat capacity of the factors (K_1); and the vertical distance AB represents the change of temperature. Hence this trigonometrical statement at once reduces to the well-known equation

$$K_2 - K_1 = \frac{U_T - U_{T+t}}{t}.$$

An important object of the discussion is to emphasize the necessity of reducing all thermochemical data to their isothermal values at some definite convenient temperature (preferably 20°), in order that they may be strictly comparable.

As an evidence of frequent laxity in this respect, the often quoted figures for the heat of neutralization of hydrochloric, hydrobromic and hydriodic acids may be cited. Thomsen records as the three values to be compared 13,740, 13,748, 13,676 calories[1] (or better, 57.46, 57.49 and 57.19 kilojoules), if the base is sodium hydroxide. On seeking the original data, it is easily found that the first corresponds to a rise of temperature from about 18° to 22°, the second to a rise from 16.6° to 18.6°, and the third to a rise from 17.5° to 19.5°. In the calculation, the approximate heat capacities of the factors were used in each of the three cases. If all these results are reduced to the isothermal value at 20°, the heats of neutralization become respectively 13,820, 13,690, and 13,650 calories (or 57.8, 57.2, and 57.1 kilojoules). The order of magnitude in the cases of hydrochloric and hydrobromic acids is reversed by the new calculation, and they have been separated by a whole per cent.[2] Even these values cannot be called ultimate, for the heat capacities of most of the solutions concerned are not accurately known, the value of Thomsen's centigrade degree in terms of the International Standard is not recorded, nor do we know how nearly the 20° points on the thermometers correspond with the true point.

It is hoped that these critical remarks will not be considered as depreciating the admirable and important work of Thomsen, Berthelot, and others. For many purposes the approximate values suffice, and if the greatest precision had been aimed at, the bulk of the results must have been much smaller, an outcome which would have been a real misfortune. In some cases the correction for cooling may have caused even a greater uncertainty than those considered above, and great care about heat capacity would have been labor thrown away. It is not at all surprising that this admirable work should not have attained a degree of

[1] "Thermochemische Untersuchungen," I, pp. 104, 155, 63, 67 (1882).

[2] The apparent inconsistency of the results on page 63 of Thomsen's work is easily explained by noting that there the heat capacity of the *product* was used in the calculation. The hydrochloric acid was in every case twice the strength of the other acids, hence the heats of dilution (which are, however, very small) should be included for an exact comparison.

accuracy sufficient for the more exacting needs of the present day.

In this connection it is appropriate to call attention to the fact that not all of the values for heat of reaction commonly given in the tables correspond to consistent atomic weights, although most of them are calculated upon the basis of O = 16.000. A praiseworthy service would be rendered by any careful computer who would take the trouble to recalculate all the data and express the results for 20° C. in terms of the most accurate table of atomic weights and the admirable c. g. s. unit of energy, the kilojoule, adopted by Ostwald.[1] The latter's preliminary tables, although an important step in the right direction, are much hampered in their usefulness by their limited scope and the frequent omission of significant decimals.

SUMMARY.

This paper is a plea for greater accuracy in the calculation of thermochemical data. The importance of a uniform temperature for comparison and consistent atomic weights are especially emphasized. It is shown that when the heat capacity of the factors is used in the calculation, the resulting heat of reaction corresponds to the final temperature attained, while if the heat capacity of the products is used in the calculation, the result corresponds to the initial temperature.

NOTES.

Note on the Occurrence of Alum as an Efflorescence on Bricks.—Some time ago I was consulted as to the cause of the discoloration of certain white bricks used in the construction of a large office building in this city. It was readily ascertained to be due to the formation and subsequent oxidation of ferrous sulphate. To remove the stain, some of the bricks were treated with sulphuric acid and then thoroughly washed with water. After they had been dried, a white efflorescence appeared on their surface, and it was found to consist for the most part of potash alum. As I have not been able to find any reference to the occurrence of this salt among the sulphates which are known to exist in similar efflorescences, it occurred to me that a quantitative analysis of the product might be of interest.

Owing to the lack of material the analysis made was incom-

[1] Ostwald's "Grundriss der Allgemeinen Chemie," p. 253 (1899).

plete, but the results proved conclusively that the water-soluble portion, which crystallized in octahedra, was nearly pure potash alum.

HARRY F. KELLER.

Rapid Determination of Molybdenum in Steel.—It has been found to be an improvement on the method previously described,[1] to use only 0.8 gram of drillings, and to make the precipitation in 200 cc. of the solution instead of 300 cc., taking only 100 cc. of the filtrate for reduction and titration. In this way an evaporation requiring more time than all the rest of the analysis put together is dispensed with. Reduction and titration should take place in small, and not in large volume of solution, on account of reduction not always being complete in the latter case, as is proved by the fact that Brakes[2] finds it necessary to use the old Emmerton factor. But if the separation be made in 200 cc. of solution, ammonia may not be used because the separation is an incomplete one with this reagent when made in a small volume of solution. The caustic soda solution is most easily made by dissolving 1 pound in 2000 to 2100 cc. water. 100 cc. of this solution is used in a determination.

Another improvement in the method (Brakes) is to expel the nitric acid used for the solution of the steel by adding 3 cc. of concentrated sulphuric acid and evaporating to fuming. The complete expulsion of the nitric acid is very important, and care must be taken that none remains on the cover, since nitrous acid or other reducing compounds are formed when a solution containing nitric acid is passed through the reductor. The results obtained by Brakes[3] indicate that chromium does not interfere with the determination when a sulphuric acid solution is used.

GEORGE AUCHY.

NEW BOOKS.

ELEMENTARY CHEMISTRY. By L. M. DENNIS AND F. W. CLARKE. New York: The American Book Company. 1902. 340 pp. LABORATORY MANUAL to accompany the above. 254 pp. Interleaved.

The matter treated in this book is essentially the same as that to be found in most other works of its class. The mode of treatment is not especially novel. It is in fact less so than in several

[1] This Journal, **24**, 273.
[2] *J. Soc. Chem. Ind.*, **21**, 832.
[3] *Loc. cit*

recent High School texts. Thus the atomic and molecular theories make their début within ten pages from the beginning, while the principle of definite proportion is reached on page 59. Even when this law appears, the phraseology suggests a dogma rather than a result of observation. Instead of demonstrating the building up of an equation from quantitative experiments, the authors show (p. 69) how, given the equation, we may calculate the results of an experiment *before* its actual performance.

The "two-volume law" (p. 96), which is not a "law" (that is, a general truth) at all, as the writers themselves tacitly acknowledge later, is used as the foundation of an elaborate proof that if we take the molecular weight of a compound and halve it, we get the density. This derivation of facts from theoretical considerations is typical of the way in which the principles of the science are handled in the book. Presently the compounds of carbon are used for illustration and the molecular weights of CH_4, C_2H_4, C_2H_2, etc., are shown to give the densities when they are divided by 2. The authors add: "In a similar way we can investigate the volatile compounds of other non-volatile elements, and prove that the two-volume law above indicated is of universal application." They have overlooked the fact that in taking the molecular weights 28 and 26 for ethylene and acetylene they were assuming the very law which they afterward hold their illustration to have proved. The maintenance of the distinction between fact and theory is the most difficult task of the teacher of chemistry. Even trained chemists find it hard. It seems to the reviewer that the present book fails to make this distinction sufficiently clear. The promise of inductive and rational treatment made in the preface is belied by much of the contents, and that at the most vital points.

The book is marred by the presence of a number of incorrect or unfortunately worded statements, such as, that when iron burns in oxygen, the melted *metal* drops to the bottom of the bottle; that ozone has a suffocating odor; that hydrogen peroxide contains "exactly twice as much oxygen" as water; that "as a solvent, water far *exceeds* every other liquid known"; and so forth. The laws "govern" regally instead of existing only so long as they are "good". The resurrection of the electrochemical series of Berzelius is strange in view of the fact that modern research has given us the means of placing the elements in the order of *chemical*

activity. Fortunately, or unfortunately, the explanation is so befogged with statements about electro-negativeness and electro-positiveness that no application, correct or incorrect, to chemical behavior is likely to be made.

The laboratory manual covers a great deal of ground. A few questions are appended to each experiment. Some quantitative experiments are given, but they are at the end of the book.

The typography, illustrations, and binding of both books are excellent. ALEXANDER SMITH.

DISINFECTION AND DISINFECTANTS. A PRACTICAL GUIDE FOR SANITARIANS, HEALTH AND QUARANTINE OFFICERS. BY M. J. ROSENAU, M.D. Philadelphia: P. Blakiston's Son and Co. 353 pp. Price, $2.00 net.

The author of this book is connected with the United States Marine Hospital Service, as Director of the Hygienic Laboratory, and has had abundant opportunity to observe practically what he has written about. The work is divided into six chapters of which the first three treat of the various disinfecting agents in general use. The opinions of the author in discussing the applicability and relative merits of the substances considered seem eminently sound and practical. The fourth chapter deals with means for destroying insects which carry diseases. The fifth chapter gives clear directions for disinfection of houses, ships, railway cars, furniture, clothing, books, etc., and is very satisfactory. The sixth and last chapter deals with the question of disinfection after special diseases, and for each one the most efficient treatment is suggested. The book is illustrated and is well printed. On the whole it may be recommended to those in need of information in this direction. J. H. LONG.

DIE ZERSETZUNG STICKSTOFFFREIER ORGANISCHER SUBSTANZEN DURCH BAKTERIEN. BY DR. O. EMMERLING. Braunschweig: Friedrich Vieweg und Sohn. 141 pp. and 7 plates. Price, 4 marks.

This little book describes the important group of decompositions usually classed as fermentations in which the active agents are not true ferments, in the modern sense of the word, but bacteria. The best known examples of such reactions are the acetic, lactic, butyric and gummy fermentations, in which carbohydrates or their derivatives are the materials on which the bacteria work. The author discusses these changes and several

others and points out the conditions under which various by-products are formed. Attention is called to the complexity of several reactions usually described in the text-books as comparatively simple. It is interesting to note in this connection the large number of cases in which ethyl alcohol is produced.

The book is not intended to be more than a suggestive compilation of results scattered through the recent literature, but as pretty full references are given it will be found useful to chemists and bacteriologists who desire to gain an insight into this important field of investigation, to which the author himself has made several valuable contributions. J. H. LONG.

G. BUNGE'S TEXT-BOOK OF PHYSIOLOGICAL AND PATHOLOGICAL CHEMISTRY. Translated by F. A. STARLING and edited by E. H. STARLING. Philadelphia: P. Blakiston's Son and Co. 1902.

Bunge's text-book still remains the most popular book on the subject. The fourth German edition, from which the second English is translated, is not much enlarged over the previous editions of the work. However, Bunge's aim was to give the general principles of the chemical side of animal physiology and pathology, and in this he succeeded most brilliantly. There are only a few questions that the author discusses in greater detail, but those are chapters of such general interest, that every biologist will read them with great pleasure, whether he does or does not accept the conclusions of the writer. Such are the chapters on vitalism and mechanism, also the chapter on alcohol. The importance for the animal organism of the mineral constituents of food is discussed by Bunge more than it has been by any other writer. The book as a whole presents in a very interesting and comprehensive form the most obscure problems of physiology, and can be recommended to those who desire to gain a general knowledge on the subject. P. A. LEVENE.

ELECTRO-CHEMICAL ANALYSIS. BY EDGAR F. SMITH. Philadelphia: P. Blakiston's Son and Company. 1902. 199 pp.

The earlier editions of Professor Smith's work on electro-chemical analysis are so widely and favorably known as to render unnecessary any extended notice of this third edition, further than to call attention to the changes and additions that have been made by the author.

The chapters on sources, reduction and measurement of cur-

rent have been slightly changed, and descriptions of new forms of apparatus have been added. Several pages are then devoted to a most interesting and suggestive description of an electrochemical laboratory. Only a few alterations have been made in the historical section, but in the special part devoted to the determination of the metals the treatment has been greatly expanded. The references to literature that are here given under each heading have been brought down to date, and many new methods and improvements of old methods have been incorporated in the text. The chapter upon the separation of the metals has been entirely rewritten, and this part of the subject is presented in a most clear and systematic form.

Both the press work and the illustrations show decided advance over the earlier editions.

It is to be regretted that in a work otherwise so complete specific mention is not made of methods for the separation of certain of the metals through the maintenance of a constant voltage, for while it is true that up to the present time such procedure has not been so far developed as to be of material assistance to the analyst, it would yet be well to call the attention of the student to the work that has been done in this field and to the possibilities of its extension. L. M. DENNIS.

A COURSE IN QUALITATIVE CHEMICAL ANALYSIS. By F. P. VENABLE. Fourth edition, revised by ALVIN S. WHEELER. New York: University Publishing Company. 1902. 54 pp. Price, 60 cents.

The only novelty that the present edition of this book offers is the absence of any reference to recent theories of solution and chemical action. The authors believe, evidently, that qualitative analysis may be taught effectively in the old way.

The directions for the systematic examination of substances are given, clearly, but so concisely, that, without the constant help of an instructor, the student will fail to secure satisfactory tests and separations. This remark applies as well, however, to larger and more pretentious text-books, and the difficulty that it points out can not be easily avoided. An index would enhance the value of the book. L. B. HALL.

RECIPES FOR THE COLOUR, PAINT, VARNISH, OIL, SOAP, AND DRY-SALTERY TRADES. Compiled by an Analytical Chemist. London: Scott, Greenwood, and Co. 1902. 336 pp. Price, $3.50 net.

Books of this class serve two purposes: they supply information

to the ignorant, and ideas or suggestions to the experienced. Every book of the sort has some things in it which will not work, and as a rule, the recipes which will work are those which have been outgrown by the special trade which used them. But if they are good in themselves, they are valuable to the non-professional; and occasionally, though rarely, those which are no good at all set the professional to thinking along a new line; at least, this has been the reviewer's experience. This book is a rather unusually good book of the sort, judging, of course, from those things which the reviewer knows. The author judiciously remarks in his preface that "it is, of course, assumed that the users of these formulae have some acquaintance with methods of manipulating them, and that they will also exercise a little common-sense when applying them to their purposes". If they do that, they will omit some of them altogether; but in the varnishes, for example, most of the recipes will make some sort of varnish, and some of them are very good, such as the coach and cabinet varnishes, though they take as many days to dry as the author gives hours. In general, the formulae are more complicated than those commonly in use in this country, and a glossary would always be useful in a book of this sort, for names vary in different countries and places, though usually intelligible to an expert. We are all acquainted, for instance, with "mineral turpentine", but no one can fail to be pleased with the idea of thinning paint with "mineral tea rose oil" instead of deodorized benzine. The reviewer commends this book to such as like books of recipes, and indorses the advice of the author to use it with some common sense. A. H. SABIN.

A COURSE IN MODERN ANALYSIS. By E. T. WHITTAKER, M.A. Cambridge: The University Press. New York: The Macmillan Co. xvi + 378 pp.

This book aims at presenting those portions of modern analysis, as based on the so-called imaginary or complex number, which "seem to be of greatest importance at the present time." Infinite series are considered in all their phases, and all those important series and functions which were developed by Fourier, Bessel, Lagrange, Legendre, Laplace, Gauss, Abel, etc., in their study of practical problems. It is a useful work for those who wish to make use of the most advanced developments of mathematical analysis in theoretical investigations of physical and chemical questions. ARTHUR S. HATHAWAY.

GENERAL PRINCIPLES OF PHYSICAL SCIENCE: AN INTRODUCTION TO THE STUDY OF THE GENERAL PRINCIPLES OF CHEMISTRY. BY ARTHUR A. NOYES. New York: Henry Holt & Co. 1902. viii + 172 pp.

While works on physical chemistry are rapidly multiplying, it is refreshing to encounter one which promises to be a distinct creation rather than a mere variation or even an improvement on its predecessors. As the present volume treats of certain parts of the subject only, an outline of its contents must be given. The first chapter, a brief one, deals mainly with the method of science. The second, also brief, discusses the fundamental concepts of physical science. The third chapter, occupying over 50 pages, treats of the general principles relating to matter. The fourth chapter, about 100 pages in length, is devoted to the general principles relating to energy. It is to be regretted that the preface does not offer any hope of the early appearance of the remaining sections dealing with the general theories of chemistry, the relations between physical properties and chemical composition, the principles relating to the occurrence and equilibrium of chemical changes, and the principles relating to the energy changes attending chemical changes.

Although the book does not deal with the whole subject of physical chemistry, it is complete in itself. While the value of the book lies largely in the sanity and symmetry of the whole treatment, a few specially excellent features may be mentioned. The unscientific patchwork of unharmonized definitions which does duty in most books on chemistry has at last been "scrapped," and it was high time that some one should undertake this task, and an inter-consistent set of definitions of the laws and terms of the science has been devised to take its place. Much care has been used in explaining the nature and relations of the various units employed in physical science. The conception of the intensity and capacity factors of the several forms of energy occupies the fundamental position in the treatment of energetics which it deserves, but has not yet received in most books in the English language. In the discussion of the laws of energetics (formerly thermodynamics), the author is remarkably successful in anticipating and avoiding or disposing of the stumbling blocks which most students of the subject encounter.

The whole treatment is scholarly in its methods and philosophical in its grasp, and at the same time it is extraordinarily

lucid. Nothing that can set each conception in the clearest light and in the most instructive relation to other conceptions seems to be forgotten. No one interested in the teaching or study of general or physical chemistry can afford to leave this book unread.

ALEXANDER SMITH.

GALVANIC BATTERIES: THEIR THEORY, CONSTRUCTION, AND USE. By S. R. BOTTONE. London and New York: Whittaker and Co. 1902. xvi + 376 pp. Price, $1.50.

The author states in his preface that this work contains a description of every known battery of any practical use along with data as to electromotive force, internal resistance, and adaptability to particular requirements. For those who may have occasion to use batteries instead of a dynamo as a source of current, the book will undoubtedly prove helpful. Although the author states that "In order to render the book useful from a scientific point of view, as well as under the practical aspect, the theory of the battery has been carefully gone into," no mention is made of theories advanced by Helmholtz and by Nernst, which have thrown such a flood of light upon the whole subject. The book is profusely illustrated and the descriptions of the construction and operation of the batteries clear and concise.

C. E. LINEBARGER.

LABORATORY EXERCISES IN PHYSICS FOR SECONDARY SCHOOLS. By GEORGE R. TWISS, B.Sc., Head of the Department of Science in the Central High School, Cleveland, Ohio. New York: The Macmillan Co. 1902. xiii + 193 pp. Price, 80 cents.

This manual is characterized by thoroughness of treatment and carefulness of statement. The author believes that "A small number of exercises worked for all there is in them" is better than a large number carelessly and superficially performed. The author has succeeded well in this his attempt *"first,* to secure the thorough enforcement of some of the fundamental principles of the science, together with a view of the kind of thinking and experimentation by means of which the facts and principles of physics have been established; *second,* to develop habits of precision in observation, thought and expression; and *third,* to train the student in the acquisition of practical power and skill in the use of apparatus."

C. E. LINEBARGER.